CHAPTER 3

RESULTS AND DISCUSSION

In this work, attempts have been made to investigate the use of seaweed (*Sargassum polyceratium*) growing naturally in the sea in Thailand as an efficient sorbent for the removal of some heavy metals in industrial wastewaters. Three parameters namely particle size, pH of solution and shaking time were optimized by means of the so-called univariate optimization method. Fully details will be discussed as follows:

3.1 Limit of Detection (LOD)[13]

The limit of detection of an analyze could be described as a concentration which gives an instrument's signal significantly different from the blank or background signal. The limit of detection can be calculated by equations (3.1-3.2).

$$\mathrm{LOD} = \frac{(3 \times S_{y/x})}{\mathrm{slope}} \qquad (3.1)$$

$$S_{y/x} = \sqrt{\frac{\sum (Yi - \hat{Y}i)^2}{n-2}} \qquad (3.2)$$

Where LOD is the limit of detection which calculated from a linear regression equation by Miller's method[13], $S_{y/x}$ is a standard deviation of y-residuals, Yi is the actual instrument response (absorbance), is $\hat{Y}_i$ the recovery absorbance which calculated from regression equation and n is the number of calibration points. The data calculation of the limit of detection was shown in Table 3.1

Table 3.1 Study of detection limit for determination of Pb(II), Cu(II), Cd(II) and Cr (III)

Number	Pb(II)		Cu(II)		Cd(II)		Cr(III)	
	Conc. (mg/g)	Abs	Conc. (mg/g)	Abs	Conc. (mg/g)	Abs	Conc. (mg/g)	Abs
1	1.0	0.011	0.5	0.031	0.5	0.075	0.5	0.031
2	2.0	0.019	1.0	0.061	1.0	0.145	1.0	0.060
3	3.0	0.029	1.5	0.091	1.5	0.198	1.5	0.085
4	4.0	0.036	2.0	0.120	2.0	0.275	2.0	0.114
5	5.0	0.045	2.5	0.147	2.5	0.333	2.5	0.137
Slope	0.087		0.582		1.290		0.532	
Intercept	0.0017		0.0027		0.0114		0.0056	
$S_{y/x}$	0.0338		0.0502		0.0983		0.0498	
R^2	0.9975		0.9995		0.9976		0.9986	
LOD(mg/l)	1.16		0.26		0.22		0.28	

3.2 Optimization of Adsorption Conditions for Dried Seaweed

3.2.1 Effect of particle size

Particle size of adsorbent has more effect on the separation of various metal ions in aqueous solutions. Therefore, it is necessary to investigate the influence of seaweed particle sizes over the ranges of 0.21-0.36, 0.36-0.60, 0.60-1.18, 1.18-2.36 mm on the separation of lead(II), copper(II), cadmium(II) and chromium(III) ions individually in aqueous solutions in order to select the appropriate seaweed particle size and use as biosorbent for binding the above four heavy metals. It was seen that the amount of adsorbed metal ion decreased as the size of the particles increased from 0.21 to 2.36 mm as shown in Table 3.2-3.5. The maximum amount of adsorbed metal ion was obtained from the particle size of 0.21-0.36 mm due to its high surface area, which is responsible for a high availability of exposed binding sites in biomass particles.[14]

The effect of seaweed particle size was investigated by varying the particle size in the range of 0.21-2.36 mm. The results were shown in Table 3.2-3.5. It was evident that the binding ability of the biosorbent was greatest for lead(II) (75%) followed by cadmium(II) (67%) then chromium(III) (65%) and copper(II) (58%). Hence, the seaweed particle size of 0.21-0.36 mm was selected as suitable sorbent for the four heavy metals studied.

Table 3.2 Effect of seaweed particle size on lead(II) adsorption by non-modified seaweed

Size (mm)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
0.21-0.36	0.1002 0.1005 0.1003	30.00 30.00 30.00	7.63 7.45 7.47	22.37 22.55 22.53	11.16 11.22 11.23	11.20±0.04	75
0.36-0.60	0.1002 0.1005 0.1008	30.00 30.00 30.00	8.57 8.44 8.36	21.43 21.56 21.64	10.70 10.72 10.73	10.72±0.02	72
0.60-1.18	0.1004 0.1003 0.1002	30.00 30.00 30.00	9.28 9.25 9.41	20.72 20.75 20.59	10.32 10.34 10.27	10.31±0.04	69
1.18-2.36	0.1004 0.1008 0.1002	30.00 30.00 30.00	10.18 9.60 10.28	19.82 20.40 19.72	9.87 10.12 9.84	9.94±0.15	68

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.3 Effect of seaweed particle size on copper(II) adsorption by non-modified seaweed

Size (mm)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
0.21-0.36	0.1003 0.1004 0.1005	7.00 7.00 7.00	3.00 2.98 2.96	4.00 4.03 4.05	1.99 2.00 2.01	2.00±0.01	58
0.36-0.60	0.1002 0.1003 0.1002	7.00 7.00 7.00	3.12 3.13 3.13	3.88 3.87 3.87	1.94 1.93 1.93	1.93±0.00	55
0.60-1.18	0.1007 0.1008 0.1009	7.00 7.00 7.00	3.35 3.41 3.39	3.65 3.59 3.62	1.81 1.78 1.79	1.79±0.02	51
1.18-2.36	0.1006 0.1003 0.1003	7.00 7.00 7.00	3.49 3.58 3.54	3.52 3.42 3.46	1.75 1.71 1.72	1.73±0.02	49

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.4 Effect of seaweed particle size on cadmium(II) adsorption by non-modified seaweed

Size (mm)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe		% Ad
					(mg/g)	$\overline{X}$	
	0.1004	5.00	1.65	3.35	1.67		
0.21-0.36	0.1002	5.00	1.69	3.31	1.65	1.66±0.01	66
	0.1005	5.00	1.66	3.34	1.66		
	0.1008	5.00	1.80	3.20	1.59		
0.36-0.60	0.1006	5.00	1.82	3.18	1.58	1.58±0.00	64
	0.1007	5.00	1.82	3.18	1.58		
	0.1002	5.00	1.98	3.02	1.51		
0.60-1.18	0.1006	5.00	1.98	3.02	1.50	1.52±0.02	60
	0.1004	5.00	1.91	3.09	1.54		
	0.1006	5.00	2.04	2.96	1.47		
1.18-2.36	0.1005	5.00	2.10	2.90	1.44	1.46±0.02	58
	0.1007	5.00	2.04	2.96	1.47		

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.5 Effect of seaweed particle size on chromium(III) adsorption by non-modified seaweed

Size (mm)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe		% Ad
					(mg/g)	$\overline{X}$	
	0.1003	10.00	3.56	6.44	3.21		
0.21-0.36	0.1002	10.00	3.55	6.45	3.22	3.24±0.04	64
	0.1003	10.00	3.42	6.58	3.28		
	0.1004	10.00	3.75	6.25	3.11		
0.36-0.60	0.1003	10.00	3.71	6.29	3.13	3.13±0.01	63
	0.1006	10.00	3.70	6.31	3.13		
	0.1003	10.00	4.31	5.69	2.84		
0.60-1.18	0.1004	10.00	4.27	5.73	2.86	2.84±0.02	57
	0.1001	10.00	4.36	5.64	2.82		
	0.1008	10.00	4.43	5.57	2.76		
1.18-2.36	0.1007	10.00	4.48	5.53	2.74	2.76±0.01	55
	0.1006	10.00	4.44	5.56	2.76		

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

3.2.2 Effect of solution pH

In general, sorption phenomena between any sorbents including biosorbents and metal ion are pH dependent. So it is very important to examine the effect of pH of solution before performing any experiments based on sorption of any metal ions on a given sorbent in order to obtain satisfactory results.

The investigation was done by varying the pH of solution in the ranges of 2.0 to 5.0. The results were shown in Tables 3.6-3.9 and Figure 3.1. The results were shown that the suitable pH of solution for lead(II), copper(II) cadmium(II) and chromium(III) were 3.5, 4.5, 4.0 and 3.0, respectively since they provided the greatest adsorption for the studied metal ions.

The effect of pH is an important parameter that affects adsorption of heavy metal ions. It may be explained in term of relation and competition effects between the H_3O^+ ions and metal ions. Metal ions that could associate with the cell wall's ligands which might have to compete with H_3O^+ ions to bind with the active sites. The polysaccharides of the cell wall provide hydroxyl group and carboxylic group. The oxygen of hydroxyl group and carboxylate ion could be available for coordination bonding with Pb(II), Cu(II), Cd(II) and Cr(III) ions in solution.[15] When pH becomes low, the concentration of H_3O^+ is higher than the concentration of metal ions. Thus, these ions occupy binding sites on the cell walls and metal ions move freely in solution. When the pH increased, the competing effect of H_3O^+ ions decreased and positively charged metal ions took up the binding sites of sorbent resulting in an increase in metal up take. Therefore experiments were not carried out beyond pH 5 to avoid heavy metal precipitated as hydroxides.[16]

Table 3.6 Effect of pH of solution on lead(II) adsorption by non-modified seaweed

pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
2.0	0.1002 0.1005 0.1004	30.00 30.00 30.00	7.85 7.72 7.78	22.15 22.28 22.22	11.05 11.09 11.07	11.07±0.02	74
2.5	0.1006 0.1003 0.1004	30.00 30.00 30.00	4.65 4.57 4.63	25.35 25.43 25.37	12.60 12.68 12.63	12.64±0.04	85
3.0	0.1001 0.1007 0.1005	30.00 30.00 30.00	4.31 4.26 4.29	25.69 25.74 25.71	12.83 12.78 12.79	12.80±0.03	86
3.5	0.1006 0.1003 0.1001	30.00 30.00 30.00	3.02 3.07 3.14	26.99 26.93 26.86	13.41 13.43 13.42	13.42±0.01	90
4.0	0.1007 0.1002 0.1008	30.00 30.00 30.00	3.19 3.20 3.17	26.81 26.80 26.83	13.31 13.37 13.31	13.33±0.03	89
4.5	0.1006 0.1003 0.1002	30.00 30.00 30.00	3.14 3.23 3.18	26.86 26.77 26.82	13.35 13.34 13.38	13.36±0.03	89
5.0	0.1009 0.1005 0.1007	30.00 30.00 30.00	3.66 3.45 3.75	26.34 26.55 26.25	13.05 13.21 13.03	13.10±0.10	89

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.7 Effect of pH of solution on copper(II) adsorption by non-modified seaweed

pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
2.0	0.1003 0.1005 0.1001	7.00 7.00 7.00	5.05 5.08 5.13	1.95 1.92 1.87	0.97 0.96 0.93	0.95±0.02	27
2.5	0.1006 0.1004 0.1002	7.00 7.00 7.00	3.03 3.04 3.08	3.97 3.96 3.92	1.98 1.97 1.96	1.97±0.01	57
3.0	0.1004 0.1003 0.1005	7.00 7.00 7.00	2.11 2.14 2.13	4.89 4.86 4.87	2.44 2.42 2.42	2.43±0.01	69
3.5	0.1006 0.1002 0.1007	7.00 7.00 7.00	2.01 2.06 1.99	4.99 4.94 5.01	2.48 2.46 2.49	2.48±0.01	71
4.0	0.1008 0.1007 0.1002	7.00 7.00 7.00	1.95 1.91 2.05	5.05 5.09 4.95	2.51 2.53 2.47	2.50±0.03	73
4.5	0.1001 0.1004 0.1003	7.00 7.00 7.00	1.96 1.82 1.83	5.04 5.18 5.17	2.52 2.58 2.58	2.56±0.03	74
5.0	0.1005 0.1007 0.1004	7.00 7.00 7.00	1.91 1.87 1.95	5.10 5.13 5.06	2.53 2.55 2.52	2.53±0.02	73

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.8 Effect of pH of solution on cadmium(II) adsorption by non-modified seaweed

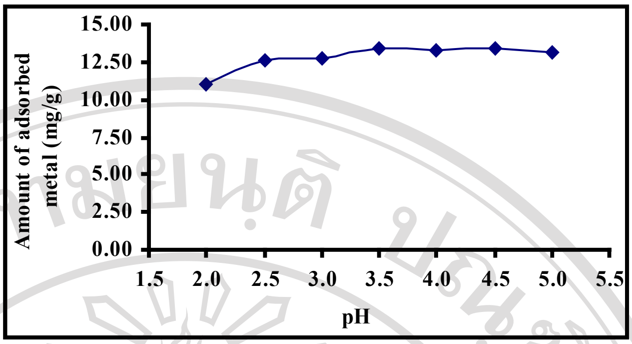
pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\bar{X}$	% Ad
2.0	0.1005 0.1004 0.1003	5.00 5.00 5.00	4.12 4.14 4.17	0.88 0.86 0.83	0.44 0.43 0.41	0.43±0.01	17
2.5	0.1007 0.1005 0.1002	5.00 5.00 5.00	2.36 2.45 2.22	2.64 2.55 2.78	1.31 1.27 1.39	1.32±0.06	51
3.0	0.1003 0.1006 0.1008	5.00 5.00 5.00	0.96 0.94 0.90	4.04 4.06 4.10	2.01 2.02 2.03	2.02±0.01	81
3.5	0.1005 0.1001 0.1006	5.00 5.00 5.00	0.61 0.63 0.61	4.39 4.37 4.39	2.19 2.18 2.18	2.18±0.00	87
4.0	0.1002 0.1003 0.1001	5.00 5.00 5.00	0.59 0.59 0.61	4.41 4.42 4.39	2.20 2.20 2.19	2.20±0.01	88
4.5	0.1003 0.1004 0.1005	5.00 5.00 5.00	0.68 0.66 0.65	4.32 4.34 4.35	2.15 2.16 2.16	2.16±0.01	87
5.0	0.1007 0.1005 0.1002	5.00 5.00 5.00	0.62 0.64 0.69	4.38 4.36 4.31	2.18 2.17 2.15	2.17±0.01	87

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

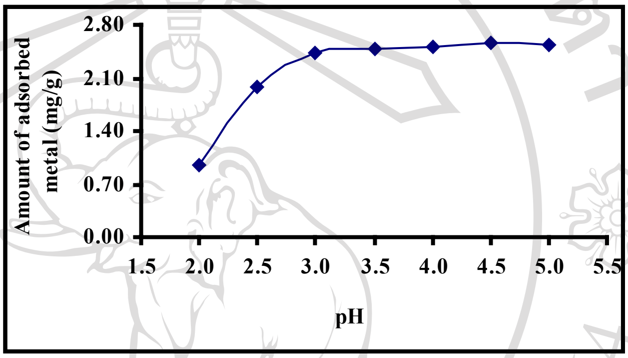
Table 3.9 Effect of pH of solution on chromium(III) adsorption by non-modified seaweed

pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
2.0	0.1003	10.00	5.45	4.55	2.27	2.25±0.03	45
	0.1004	10.00	5.54	4.46	2.22		
	0.1001	10.00	5.45	4.55	2.27		
2.5	0.1005	10.00	2.48	7.52	3.74	3.70±0.03	74
	0.1003	10.00	2.62	7.38	3.68		
	0.1002	10.00	2.60	7.40	3.69		
3.0	0.1008	10.00	2.38	7.62	3.78	3.82±0.04	77
	0.1004	10.00	2.31	7.69	3.83		
	0.1006	10.00	2.22	7.78	3.87		
3.5	0.1007	10.00	4.46	5.54	2.75	2.72±0.03	54
	0.1002	10.00	4.59	5.41	2.70		
	0.1002	10.00	4.57	5.43	2.71		
4.0	0.1005	10.00	4.48	5.52	2.75	2.77±0.02	56
	0.1004	10.00	4.41	5.59	2.78		
	0.1007	10.00	4.41	5.59	2.78		
4.5	0.1003	10.00	4.41	5.59	2.79	2.86±0.13	61
	0.1008	10.00	3.93	6.07	3.01		
	0.1003	10.00	4.41	5.59	2.79		
5.0	0.1004	10.00	5.80	4.20	2.09	2.18±0.15	42
	0.1005	10.00	5.79	4.21	2.09		
	0.1006	10.00	5.26	4.74	2.36		

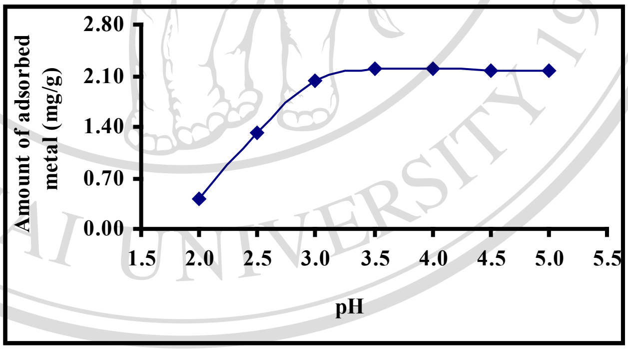
Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption



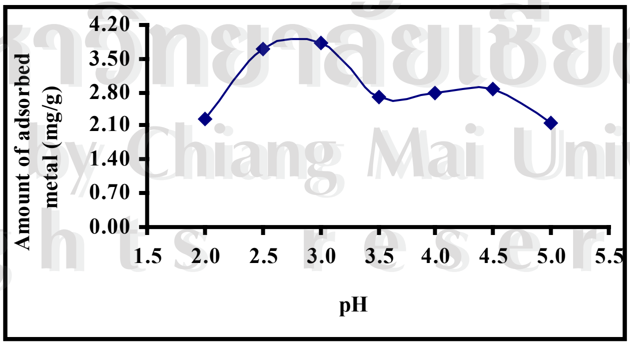
(a)



(b)



(c)



(d)

Figure 3.1 Effect of pH of solution on (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) adsorption by non-modified seaweed

3.2.3 Effect of shaking time

In any sorption process, based on sorption of metal ions on any sorbents; it is necessary to shake the solution at the appropriate period of time in order to study the equilibrium of the sorption. In this experiment the shaking time of solution was performed in the range of 5 to 120 min at speed of 200 rpm. The results obtained were shown in Tables 3.10-3.13 and Figure 3.2.

Table 3.10 Effect of shaking time on lead(II) adsorption by non-modified seaweed

Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe		% Ad
					(mg/g)	$\overline{X}$	
5	0.1004	30.00	9.43	20.57	10.24	10.25±0.08	69
	0.1008	30.00	9.16	20.84	10.34		
	0.1002	30.00	9.62	20.38	10.17		
10	0.1002	30.00	6.93	23.07	11.51	11.51±0.01	77
	0.1003	30.00	6.94	23.06	11.49		
	0.1005	30.00	6.85	23.15	11.52		
20	0.1007	30.00	5.18	24.82	12.32	12.32±0.00	83
	0.1006	30.00	5.21	24.79	12.32		
	0.1007	30.00	5.20	24.80	12.31		
30	0.1008	30.00	4.58	25.42	12.61	12.62±0.05	84
	0.1005	30.00	4.73	25.27	12.57		
	0.1006	30.00	4.49	25.51	12.68		
60	0.1005	30.00	3.64	26.36	13.11	13.10±0.02	88
	0.1006	30.00	3.69	26.31	13.08		
	0.1008	30.00	3.55	26.45	13.12		
90	0.1009	30.00	3.50	26.50	13.13	13.10±0.05	88
	0.1005	30.00	3.61	26.39	13.13		
	0.1006	30.00	3.74	26.26	13.05		
120	0.1004	30.00	3.64	26.37	13.13	12.79±0.57	88
	0.1005	30.00	3.65	26.35	13.11		
	0.1007	30.00	5.58	24.42	12.12		

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.11 Effect of shaking time on copper(II) adsorption by non-modified seaweed

Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
5	0.1002	7.00	5.01	1.99	0.99	0.89±0.11	25
	0.1004	7.00	5.22	1.78	0.88		
	0.1001	7.00	5.44	1.56	0.78		
10	0.1007	7.00	4.05	2.95	1.46	1.41±0.06	40
	0.1005	7.00	4.19	2.81	1.40		
	0.1002	7.00	4.28	2.72	1.36		
20	0.1008	7.00	3.04	3.96	1.97	1.90±0.06	55
	0.1004	7.00	3.18	3.82	1.90		
	0.1002	7.00	3.31	3.69	1.84		
30	0.1005	7.00	2.33	4.67	2.32	2.26±0.07	65
	0.1006	7.00	2.45	4.56	2.26		
	0.1003	7.00	2.63	4.37	2.18		
60	0.1003	7.00	1.95	5.05	2.52	2.52±0.01	72
	0.1001	7.00	1.98	5.02	2.51		
	0.1006	7.00	1.92	5.08	2.52		
90	0.1002	7.00	1.96	5.04	2.52	2.54±0.03	73
	0.1008	7.00	1.87	5.13	2.54		
	0.1007	7.00	1.83	5.17	2.57		
120	0.1006	7.00	1.94	5.06	2.52	2.52±0.01	72
	0.1003	7.00	1.96	5.04	2.51		
	0.1008	7.00	1.89	5.11	2.53		

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.12 Effect of shaking time on cadmium(II) adsorption by non-modified seaweed

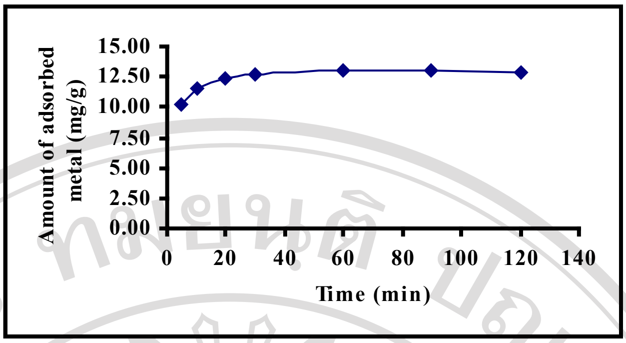
Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\bar{X}$	% Ad
5	0.1005 0.1003 0.1002	5.00 5.00 5.00	3.37 3.33 3.62	1.63 1.67 1.38	0.81 0.83 0.69	0.78±0.08	33
10	0.1002 0.1003 0.1006	5.00 5.00 5.00	2.55 2.70 2.35	2.45 2.30 2.65	1.22 1.15 1.32	1.23±0.08	46
20	0.1004 0.1005 0.1007	5.00 5.00 5.00	1.95 1.92 1.87	3.05 3.08 3.13	1.52 1.53 1.55	1.53±0.02	62
30	0.1003 0.1004 0.1005	5.00 5.00 5.00	0.95 0.94 0.94	4.05 4.06 4.06	2.02 2.02 2.02	2.02±0.00	81
60	0.1007 0.1004 0.1006	5.00 5.00 5.00	0.68 0.86 0.75	4.32 4.14 4.25	2.15 2.06 2.11	2.11±0.04	83
90	0.1003 0.1002 0.1004	5.00 5.00 5.00	0.66 0.60 0.64	4.34 4.40 4.36	2.17 2.20 2.17	2.18±0.02	88
120	0.1006 0.1007 0.1004	5.00 5.00 5.00	0.67 0.61 0.63	4.33 4.39 4.37	2.15 2.18 2.18	2.17±0.02	88

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

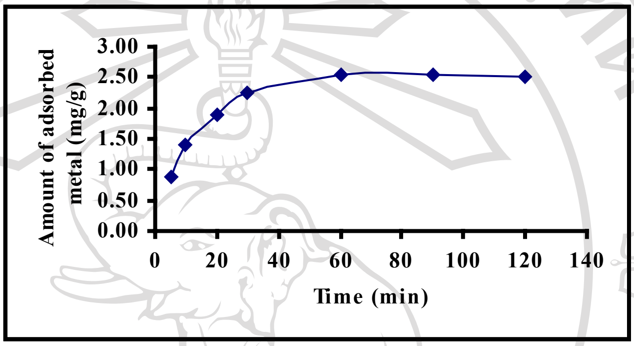
Table 3.13 Effect of shaking time on chromium(III) adsorption by non-modified seaweed

Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\bar{X}$	% Ad
5	0.1002 0.1005 0.1004	10.00 10.00 10.00	5.61 5.36 5.45	4.39 4.64 4.55	2.19 2.31 2.27	2.26±0.06	46
10	0.1007 0.1004 0.1003	10.00 10.00 10.00	4.15 4.21 4.30	5.85 5.79 5.70	2.90 2.88 2.84	2.88±0.03	58
20	0.1005 0.1007 0.1004	10.00 10.00 10.00	3.20 3.18 3.26	6.80 6.82 6.74	3.38 3.38 3.36	3.37±0.01	68
30	0.1007 0.1009 0.1006	10.00 10.00 10.00	2.79 2.67 2.76	7.21 7.33 7.24	3.58 3.63 3.60	3.60±0.03	73
60	0.1003 0.1002 0.1002	10.00 10.00 10.00	2.42 2.53 2.55	7.58 7.47 7.45	3.78 3.73 3.72	3.74±0.03	75
90	0.1006 0.1006 0.1004	10.00 10.00 10.00	2.56 2.57 2.69	7.44 7.43 7.32	3.70 3.69 3.64	3.68±0.03	74
120	0.1002 0.1005 0.1004	10.00 10.00 10.00	2.78 2.60 2.65	7.22 7.40 7.35	3.60 3.68 3.66	3.65±0.04	74

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption



(a)



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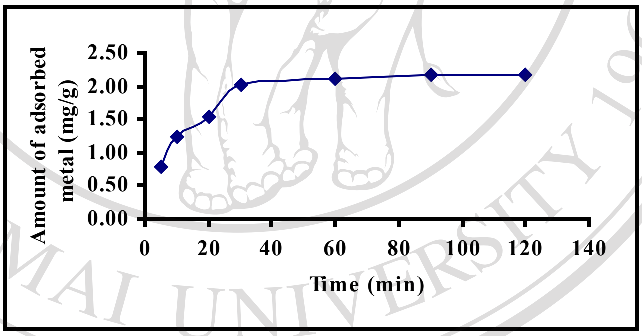

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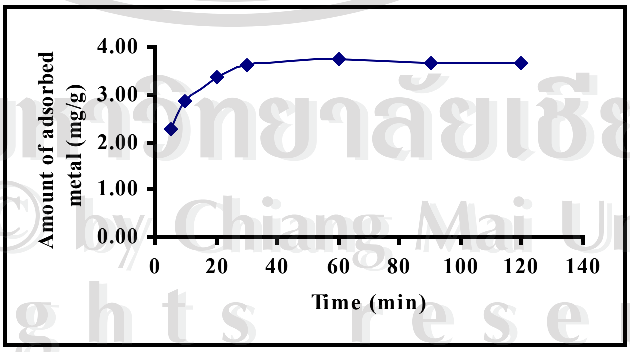


(d)

Figure 3.2 Effect of shaking time on (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) adsorption by non-modified seaweed

The amounts of adsorbed metal ions increased rapidly within the first 30 min. After that, the amount of adsorbed metals rose slowly before going equilibrium. In this experiment, the time to reach adsorption equilibrium was 60 min for all four metal ions. The shaking time depends on kinetics of metal adsorption in the same way of adsorption rate depends on the physical adsorption on the cell surface. The adsorption rate of metal can be explained by the movement of metal ion. The metal ions in the solution can move to the empty surface of seaweed very rapidly at the early stage. After the metal ions have been built up at the adsorption site on the surface of seaweed, a further movement of metal ions from solution would be retarded due to filled of binding sites. In early state, probability of contact between sorbent and sorbate is high. This may cause high rate of adsorption at the initial state. However, there are several parameters that determine the adsorption rate. Such as stirring rate of the aqueous phase, properties of sorbent and properties of metal ions.[17] At equilibrium, the adsorption of metal ions on the non-modified seaweed is greatest for lead(II) (88%) followed by cadmium(II) (87%) then chromium(III) (75%) and copper (II) (72%) indicating that the non-modified seaweed could be used as an efficient adsorbent for the above four heavy metals studied. Simultaneous removal of lead(II), copper(II), cadmium(II) and chromium(III) using the non-modified seaweeds are proven to be possible.

3.2.4 Effect of other metals

Previous experiments described in sections 3.2.1-3.2.3 revealed that the use of non-modified seaweed for the removal of lead(II), copper(II), cadmium(II) and chromium(III) simultaneously would be possible. Attempts were made to examine effects of other metals on the separation of each metal ion using the non-modified seaweed as biosorbent. Other metals affecting the adsorption of metal of interest were summarized in Table 3.14-3.17. It was found that the higher concentration of competitive metal ions added, the lower adsorption efficiency of target ions yield by non-modified seaweed. The results also show that this biosorbent could remove more than one metallic species simultaneously which would be important in wastewater treatment processes.[18]

The amount of each kind of metal ions (Pb, Cd, Cu or Cr) sorbed on the non-modified biosorbent from the aqueous solutions in the presence of the other three metal ions is the greatest for lead(II) (4.46-3.09 mg/g) followed by chromium(III) (3.72-2.58 mg/g) then cadmium(II) (3.56-2.92 mg/g) and copper(II) (3.06-2.76 mg/g) depending on the weight ratio of the metal ions concerned (i.e., target ion : the other three ions = 1.0:0.5:0.5:0.5, 1.0:1.0:1.0:1.0, 1.0:1.5:1.5:1.5).

In the binary mixture, the metal ions uptake by the biosorbent are according to the following decreasing order: Pb(II) (4.70-4.19 mg/g) > Cr(III) (3.94-2.96 mg/g) > Cd(II) (3.86-3.42 mg/g) > Cu(II) (3.23-3.01 mg/g).

For ternary mixture, the metal ions uptake by the biosorbent are according to the following decreasing order: Pb(II) (4.66-3.60 mg/g) > Cr(III) (3.78-3.05 mg/g) > Cd(II) (3.85-3.04 mg/g) > Cu(II) (3.11-2.78 mg/g).

Table 3.14 Effect of copper(II), cadmium(II) and chromium(III) on lead(II) adsorption

Target metal : competitive metals Ratio	Amount of Pb(II) adsorbed (mg/g)	Average amount of Pb(II) adsorbed (mg/g)	% Adsorption efficiency
Pb(II)	4.70 4.74 4.74	4.72	-
Pb(II):Cu(II) 1.0 : 0.5	4.65 4.67 4.68	4.67	-1
Pb(II):Cu(II) 1.0 : 1.0	4.27 4.36 4.40	4.34	-8
Pb(II):Cu(II) 1.0 : 1.5	4.26 4.26 4.27	4.27	-10
Pb(II):Cr(III) 1.0 : 0.5	4.28 4.51 4.53	4.44	-6
Pb(II):Cr(III) 1.0 : 1.0	4.32 4.32 4.31	4.31	-9
Pb(II):Cr(III) 1.0 : 1.5	4.18 4.19 4.20	4.19	-11
Pb(II):Cd(II) 1.0 : 0.5	4.68 4.71 4.72	4.70	-
Pb(II):Cd(II) 1.0 : 1.0	4.42 4.33 4.34	4.36	-7
Pb(II):Cd(II) 1.0 : 1.5	4.23 4.32 4.24	4.26	-10

Table 3.14 Effect of copper(II), cadmium(II) and chromium(III) on lead(II) adsorption (continue)

Target metal : competitive metals Ratio	Amount of Pb(II) adsorbed (mg/g)	Average amount of Pb(II) adsorbed (mg/g)	% Adsorption efficiency
Pb(II): Cd(II):Cu(II) 1.0 : 0.5 : 0.5	4.49 4.48 4.48	4.48	-5
Pb(II): Cd(II):Cu(II) 1.0 : 1.0 : 1.0	4.30 4.31 4.31	4.31	-9
Pb(II): Cd(II):Cu(II) 1.0 : 1.5 : 1.5	3.69 3.70 3.71	3.70	-22
Pb(II):Cr(III):Cu(II) 1.0 : 0.5 : 0.5	4.51 4.50 4.52	4.51	-4
Pb(II):Cr(III):Cu(II) 1.0 : 1.0 : 1.0	4.27 4.25 4.24	4.25	-10
Pb(II):Cr(III):Cu(II) 1.0 : 1.5 : 1.5	3.61 3.61 3.63	3.62	-23
Pb(II):Cr(III):Cd(II) 1.0 : 0.5 : 0.5	4.68 4.64 4.66	4.66	-1
Pb(II):Cr(III):Cd(II) 1.0 : 1.0 : 1.0	4.00 4.02 4.04	4.03	-15
Pb(II):Cr(III):Cd(II) 1.0 : 1.5 : 1.5	3.62 3.62 3.56	3.60	-24
Pb(II):Cr(III):Cd(II):Cu(II) 1.0 : 0.5 : 0.5 : 0.5	4.47 4.44 4.46	4.46	-5
Pb(II):Cr(III):Cd(II):Cu(II) 1.0 : 1.0 : 1.0 : 1.0	4.00 4.06 4.05	4.04	-14
Pb(II):Cr(III):Cd(II):Cu(II) 1.0 : 1.5 : 1.5 : 1.5	3.10 3.11 3.06	3.09	-34

Table 3.15 Effect of lead(II), cadmium(II) and chromium(III) on copper(II) adsorption

Target metal : competitive metals Ratio	Amount of Cu(II) adsorbed (mg/g)	Average amount of Cu(II) adsorbed (mg/g)	% Adsorption efficiency
Cu(II)	3.81 3.83 3.86	3.84	-
Cu(II):Cr(III) 1.0 : 0.5	3.14 3.17 3.11	3.14	-18
Cu(II):Cr(III) 1.0 : 1.0	2.93 2.98 3.04	2.98	-22
Cu(II):Cr(III) 1.0 : 1.5	2.86 2.92 2.93	2.91	-24
Cu(II):Cd(II) 1.0 : 0.5	3.12 3.11 3.13	3.12	-18
Cu(II):Cd(II) 1.0 : 1.0	3.20 3.28 3.21	3.23	-16
Cu(II):Cd(II) 1.0 : 1.5	3.02 3.01 3.00	3.01	-21
Cu(II):Pb(II) 1.0 : 0.5	3.14 3.15 3.12	3.14	-18
Cu(II):Pb(II) 1.0 : 1.0	3.17 3.18 3.24	3.19	-17
Cu(II):Pb(II) 1.0 : 1.5	3.12 3.13 3.16	3.14	-18
Cu(II):Pb(II): Cd(II) 1.0 : 0.5 : 0.5	3.08 3.09 3.06	3.07	-20
Cu(II):Pb(II): Cd(II) 1.0 : 1.0 : 1.0	2.90 2.82 2.83	2.85	-26
Cu(II):Pb(II): Cd(II) 1.0 : 1.5 : 1.5	2.98 2.96 2.95	2.96	-23

Table 3.15 Effect of lead(II), cadmium(II) and chromium(III) on copper(II) adsorption (continue)

Target metal : competitive metals Ratio	Amount of Cu(II) adsorbed (mg/g)	Average amount of Cu(II) adsorbed (mg/g)	% Adsorption efficiency
Cu(II):Pb(II):Cr(III) 1.0 : 0.5 : 0.5	3.09 3.13 3.12	3.11	-19
Cu(II):Pb(II):Cr(III) 1.0 : 1.0 : 1.0	2.99 2.99 2.95	2.98	-22
Cu(II):Pb(II):Cr(III) 1.0 : 1.5 : 1.5	3.02 3.01 3.08	3.03	-21
Cu(II):Cr(III):Cd(II) 1.0 : 0.5 : 0.5	3.06 3.07 3.10	3.07	-20
Cu(II):Cr(III):Cd(II) 1.0 : 1.0 : 1.0	2.84 2.73 2.77	2.78	-27
Cu(II):Cr(III):Cd(II) 1.0 : 1.5 : 1.5	2.86 2.86 2.85	2.86	-25
Cu(II):Pb(II):Cr(III):Cd(II) 1.0 : 0.5 : 0.5 : 0.5	3.06 3.08 3.05	3.06	-20
Cu(II):Pb(II):Cr(III):Cd(II) 1.0 : 1.0 : 1.0 : 1.0	2.85 2.84 2.86	2.85	-26
Cu(II):Pb(II):Cr(III):Cd(II) 1.0 : 1.5 : 1.5 : 1.5	2.77 2.75 2.76	2.76	-28

Table 3.16 Effect of lead(II), copper(II) and chromium(III) on cadmium(II) adsorption

Target metal : competitive metals Ratio	Amount of Cd(II) adsorbed (mg/g)	Average amount of Cd(II) adsorbed (mg/g)	% Adsorption efficiency
Cd(II)	3.86 3.83 3.89	3.86	-
Cd(II):Cr(III) 1.0 : 0.5	3.68 3.69 3.70	3.69	-4
Cd(II):Cr(III) 1.0 : 1.0	3.55 3.52 3.64	3.57	-7
Cd(II):Cr(III) 1.0 : 1.5	3.41 3.44 3.42	3.42	-11
Cd(II):Cu(II) 1.0 : 0.5	3.80 3.79 3.86	3.82	-1
Cd(II):Cu(II) 1.0 : 1.0	3.69 3.66 3.73	3.69	-4
Cd(II):Cu(II) 1.0 : 1.5	3.45 3.46 3.46	3.46	-10
Cd(II):Pb(II) 1.0 : 0.5	3.86 3.87 3.85	3.86	-
Cd(II):Pb(II) 1.0 : 1.0	3.71 3.72 3.69	3.71	-4
Cd(II):Pb(II) 1.0 : 1.5	3.70 3.73 3.74	3.72	-3
Cd(II):Pb(II): Cu(II) 1.0 : 0.5 : 0.5	3.82 3.86 3.86	3.85	-
Cd(II):Pb(II): Cu(II) 1.0 : 1.0 : 1.0	3.47 3.19 3.38	3.34	-13
Cd(II):Pb(II): Cu(II) 1.0 : 1.5 : 1.5	3.33 3.31 3.30	3.31	-14

Table 3.16 Effect of lead(II), copper(II) and chromium(III) on cadmium(II) adsorption (continue)

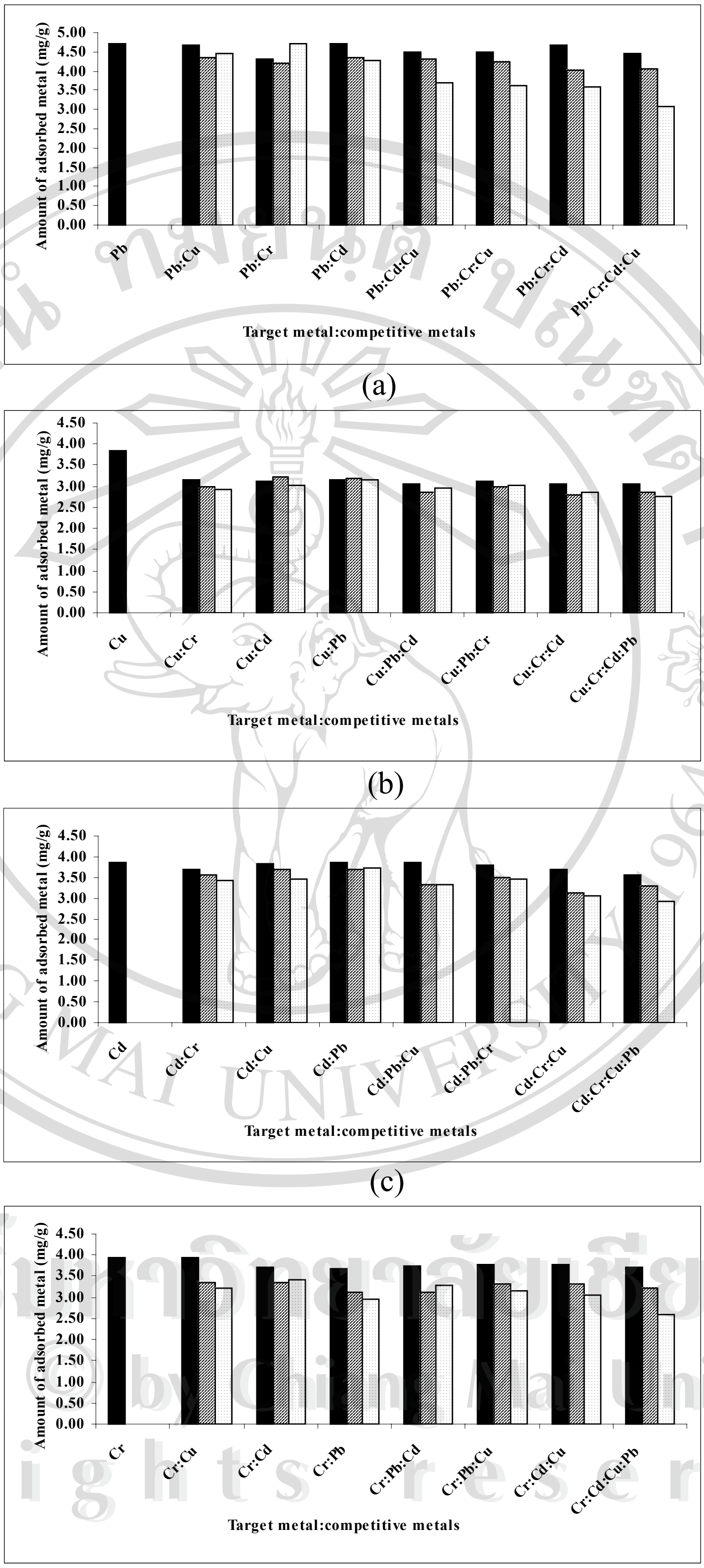
Target metal : competitive metals Ratio	Amount of Cd(II) adsorbed (mg/g)	Average amount of Cd(II) adsorbed (mg/g)	% Adsorption efficiency
Cd(II):Pb(II):Cr(III) 1.0 : 0.5 : 0.5	3.79 3.78 3.76	3.78	-2
Cd(II):Pb(II):Cr(III) 1.0 : 1.0 : 1.0	3.57 3.34 3.58	3.50	-9
Cd(II):Pb(II):Cr(III) 1.0 : 1.5 : 1.5	3.45 3.44 3.49	3.46	-10
Cd(II):Cr(III):Cu(II) 1.0 : 0.5 : 0.5	3.70 3.69 3.71	3.70	-4
Cd(II):Cr(III):Cu(II) 1.0 : 1.0 : 1.0	3.19 3.06 3.13	3.13	-19
Cd(II):Cr(III):Cu(II) 1.0 : 1.5 : 1.5	3.05 3.04 3.03	3.04	-21
Cd(II):Pb(II):Cr(III):Cu(II) 1.0 : 0.5 : 0.5 : 0.5	3.57 3.56 3.55	3.56	-8
Cd(II):Pb(II):Cr(III):Cu(II) 1.0 : 1.0 : 1.0 : 1.0	3.65 3.11 3.08	3.28	-15
Cd(II):Pb(II):Cr(III):Cu(II) 1.0 : 1.5 : 1.5 : 1.5	2.88 2.91 2.96	2.92	-24

Table 3.17 Effect of lead(II), copper(II) and cadmium(II) on chromium(III) adsorption

Target metal : competitive metals Ratio	Amount of Cr(III) adsorbed (mg/g)	Average amount of Cr(III) adsorbed (mg/g)	% Adsorption efficiency
Cr(III)	3.89 3.94 3.96	3.93	-
Cr(III):Cu(II) 1.0 : 0.5	3.87 3.77 3.87	3.84	-2
Cr(III):Cu(II) 1.0 : 1.0	3.30 3.36 3.37	3.34	-15
Cr(III):Cu(II) 1.0 : 1.5	3.24 3.24 3.20	3.23	-18
Cr(III):Cd(II) 1.0 : 0.5	3.70 3.78 3.68	3.72	-5
Cr(III):Cd(II) 1.0 : 1.0	3.33 3.32 3.38	3.34	-15
Cr(III):Cd(II) 1.0 : 1.5	3.43 3.42 3.40	3.42	-13
Cr(III):Pb(II) 1.0 : 0.5	3.79 3.50 3.78	3.69	-10
Cr(III):Pb(II) 1.0 : 1.0	3.10 3.12 3.12	3.11	-21
Cr(III):Pb(II) 1.0 : 1.5	2.98 2.96 2.95	2.96	-23
Cr(III):Pb(II): Cd(II) 1.0 : 0.5 : 0.5	3.75 3.74 3.76	3.75	-5
Cr(III):Pb(II): Cd(II) 1.0 : 1.0 : 1.0	3.11 3.10 3.12	3.11	-21
Cr(III):Pb(II): Cd(II) 1.0 : 1.5 : 1.5	3.29 3.26 3.27	3.28	-17

Table 3.17 Effect of lead(II), copper(II) and cadmium(II) on chromium(III) adsorption (continue)

Target metal : competitive metals Ratio	Amount of Cr (III) adsorbed (mg/g)	Average Amount of Cr(III) adsorbed (mg/g)	% Adsorption efficiency
Cr(III):Pb(II):Cu(II) 1.0 : 0.5 : 0.5	3.76 3.79 3.78	3.78	-4
Cr(III):Pb(II):Cu(II) 1.0 : 1.0 : 1.0	3.30 3.32 3.35	3.33	-15
Cr(III):Pb(II):Cu(II) 1.0 : 1.5 : 1.5	3.13 3.14 3.16	3.15	-20
Cr(III):Cd(II):Cu(II) 1.0 : 0.5 : 0.5	3.76 3.78 3.79	3.78	-4
Cr(III):Cd(II):Cu(II) 1.0 : 1.0 : 1.0	3.34 3.30 3.32	3.32	-16
Cr(III):Cd(II):Cu(II) 1.0 : 1.5 : 1.5	3.02 3.01 3.11	3.05	-22
Cr(III):Pb(II):Cd(II):Cu(II) 1.0 : 0.5 : 0.5 : 0.5	3.75 3.71 3.69	3.72	-5
Cr(III):Pb(II):Cd(II):Cu(II) 1.0 : 1.0 : 1.0 : 1.0	3.22 3.21 3.22	3.22	-18
Cr(III):Pb(II):Cd(II):Cu(II) 1.0 : 1.5 : 1.5 : 1.5	2.54 2.59 2.60	2.58	-34



(d)

Figure 3.3 Effect of competitive metals on (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) adsorption by non-modified seaweed

Target:Competitive = 1.0:0.5 Target:Competitive = 1.0:1.0 Target:Competitive = 1.0:1.5

3.2.5 Isotherm character for dried seaweed

Certain constant values of the express surface properties and affinity of the sorbent characterize the adsorption isotherm. It can also used to compare adsorption capacity of biomass in hetero ions system. Out of several isotherm equations, two of which have been applied for this study, the Freundlich and Langmuir isotherms.

The adsorption isotherm was investigated at various concentrations of lead(II) (30.00-50.00 mg/l), copper(II) (5.00-30.00 mg/l), cadmium(II) (10.00-50.00 mg/l) and chromium(III) (5.00-25.00 mg/l), respectively. The Langmuir and Freundlich adsorption isotherms of each metal ion for non-modified seaweed were shown in Figures 3.4-3.5.

As described in chapter 1, isotherm data obtained from the experiment will be converted to Langmuir and Freudlich equations. The regression coefficients are used as a criterion to consider the type of adsorption. The results of R^2 shown in Figure 3.4 - 3.5 of Langmuir and Freudlich isotherm are grater than 0.97. This can be concluded that the type of adsorption can be ascribed to both Langmuir and Freudlich models.

The Langmuir adsorption isotherm has traditionally been used to quantify and performance of biosorbent. In its formulation, binding to the surface was primarily by physical forces and implicit in its derivation which was the assumption that all sites possess equal affinity for the adsorbate. It was extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase. In chapter1, Q^o is amount of metal adsorbed per gram of dried seaweed forming a complete monolayer on the surface and b is Langmuir adsorption constant. Langmuir adsorption theory requires that adsorption is limited to the formation of a monolayer and all surface sites have the same energy or equal affinity for the adsorbate. High values of b are reflected by the steep initial slope of a sorption isotherm and indicate a high affinity for the adsorbate. In terms of implementation, biosorbents with the highest possible Q^o and a high value of b are the most desirable.

The Freudlich isotherm is originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation. Specifically, the Freudlich isotherm is obtained when a log-normal affinity distribution is assumed. Where K_F and n are empirically determined constants, with K_F being related to the maximum binding capacity, and n related to the affinity or binding strength.[19]

The adsorption phenomena can be describes by the two differentiation isotherms. Langmuir isotherm indicated the mono-layer surface binding. At lower concentration of sorbate tends to bind with sites of sorbent in one layer. At the high concentration of sorbate the Freudlich isotherm is used to explain the multi-layer adsorption phenomena.

Table 3.18 Adsorption of lead(II) by non-modified seaweed

C_i (mg/l)	C_e (mg/l)	qe (mg/g)	$1/C_e$	1/qe	log C_e	log qe
30.00	2.40	13.74	0.42	0.07	0.38	1.14
35.00	2.85	16.01	0.35	0.06	0.46	1.20
40.00	3.22	18.34	0.31	0.05	0.51	1.27
45.00	3.61	20.60	0.28	0.05	0.56	1.31
50.00	4.21	22.81	0.24	0.04	0.63	1.36

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed

Table 3.19 Adsorption of copper(II) by non-modified seaweed

C_i (mg/l)	C_e (mg/l)	qe (mg/g)	$1/C_e$	1/qe	log C_e	log qe
5.00	1.55	1.72	0.65	0.58	0.19	0.24
7.00	1.92	2.53	0.52	0.40	0.28	0.40
10.00	2.81	3.59	0.36	0.28	0.45	0.56
15.00	3.87	5.54	0.26	0.18	0.59	0.74
20.00	2.22	7.21	0.18	0.14	0.74	0.86
30.00	8.07	10.92	0.12	0.09	0.91	1.04

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed

Table 3.20 Adsorption of cadmium(II) by non-modified seaweed

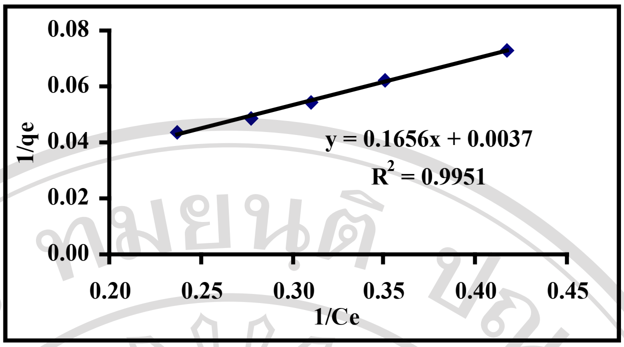
C_i (mg/l)	C_e (mg/l)	qe (mg/g)	$1/C_e$	1/qe	log C_e	log qe
10.00	2.12	4.01	0.47	0.25	0.33	0.60
15.00	3.49	5.82	0.29	0.17	0.54	0.77
20.00	5.54	7.31	0.18	0.14	0.74	0.86
30.00	9.59	10.18	0.10	0.10	0.98	1.00
40.00	13.64	13.13	0.07	0.08	1.14	1.12
50.00	16.29	16.79	0.06	0.06	1.21	1.23

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed

Table 3.21 Adsorption of chromium(III) by non-modified seaweed

C_i (mg/l)	C_e (mg/l)	qe (mg/g)	$1/C_e$	1/qe	log C_e	log qe
5.00	1.09	1.95	0.92	0.51	0.04	0.29
10.00	3.14	3.42	0.32	0.29	0.50	0.53
15.00	6.65	4.15	0.15	0.24	0.82	0.62
20.00	10.99	4.48	0.09	0.22	1.04	0.65
25.00	15.04	4.95	0.07	0.20	1.18	0.70

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed,



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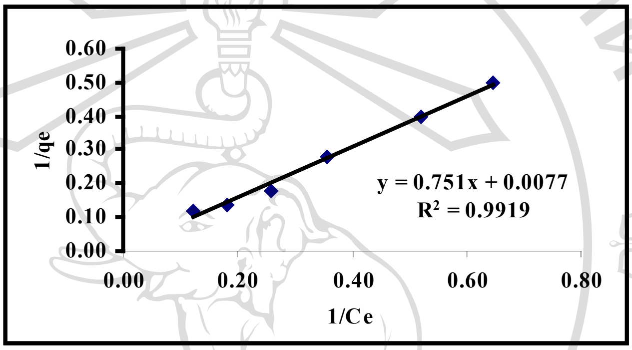

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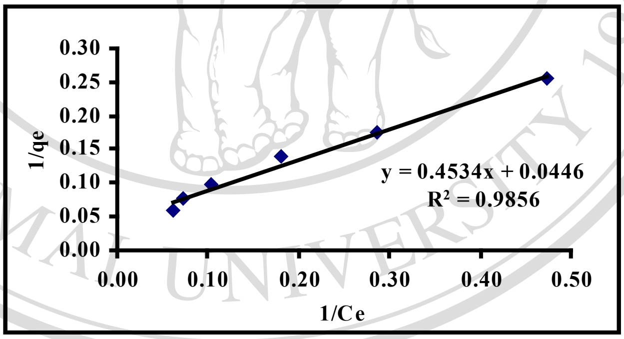
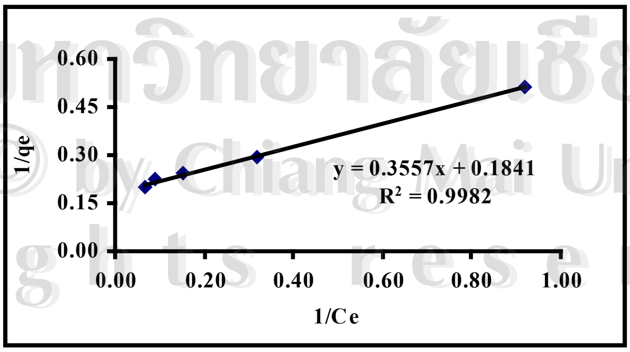


(c)



(d)

Figure 3.4 Langmuir adsorption isotherm of (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) by non-modified seaweed

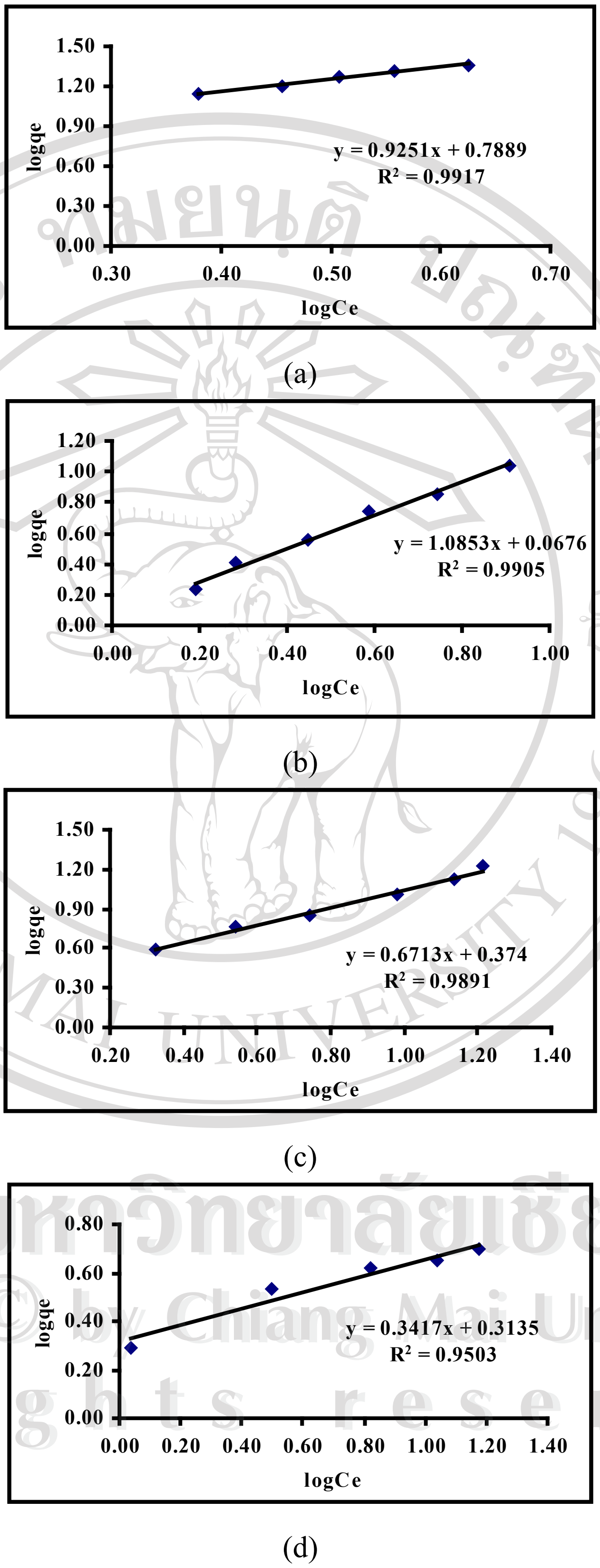


Figure 3.5 Freundlich adsorption isotherm of (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) by non-modified seaweed

Table 3.22 A comparison of Langmuir adsorption constants between each metal using non-modified seaweed as a sorbent

Metal	The Langmuir adsorption constants		
	Q^o	b	R^2
Lead(II)	270.27	0.02	0.9951
Copper(II)	129.87	0.01	0.9919
Cadmium(II)	21.98	0.10	0.9850
Chromium(III)	5.43	0.52	0.9982

Q^o: amount of metal adsorbed per gram of dried seaweed forming a complete monolayer on the surface (mg/g)

b: Langmuir adsorption constant,
R^2: correlation coefficient

Table 3.23 A comparison of Freundlich adsorption constants between each metal using non-modified seaweed as a sorbent

Metal	The Freundlich adsorption constants		
	K_F	n	R^2
Lead(II)	6.15	1.08	0.9917
Copper(II)	1.17	0.92	0.9905
Cadmium(II)	2.37	1.49	0.9891
Chromium(III)	2.06	2.93	0.9503

R^2: correlation coefficient
K_F : Freundlich constant representing adsorption capacity
n: Freundlich constant representing adsorption intensity

3.3 The Optimization of Adsorption Conditions for Modified Seaweed

The dried seaweed powder with optimum sizes (0.21-0.36 mm) as previously described in section 3.2.1 was chemically modified by crosslink-xanthate method. The modified seaweed was used as biosorbent for the removal of Pb(II), Cu(II), Cd (II) and Cr(III). Optimum conditions for the adsorption of some heavy metal ions (Pb, Cu, Cd and Cr) were investigated by univariate method as described earlier with the non-modified seaweed (section 3.2).

3.3.1 Effect of initial pH of solution

The effect of initial pH of solution was examined by varying the initial pH of solution in the range of 2.0-5.0. The results obtained were shown in Tables 3.24-3.27 and Figure 3.6. It was found that the suitable pH of solution for lead(II), chromium(III) copper(II) and cadmium(II) were 3.5, 3.0, 3.5 and 3.5, respectively which were different from those obtained with the non-modified seaweed(3.5, 4.5, 4.0 and 3.0, respectively). The explanation for this might be due to the fact that the functional group of the surface of the modified seaweed is changed from organic substrate to xanthate which acted as cation exchanger with Na^+ form. So the pH of solution required for binding the four heavy metals is altered. Refer back to Tables 3.24-3.27 and Figure 3.6, it is shown that the adsorption of the four metal ions studied on the modified seaweed is greatest for lead(II) (91%) followed by cadmium(II) (91%) then copper(II) (86%) and chromium(III) (86%). By comparison with those obtained with the non-modified seaweed the binding ability of the biosorbent is according to the following decreasing order: Pb(II) (90%) > Cd(II) (88%) > Cr(III) (77%) > Cu(II) (74%). For the modified seaweed, the binding ability sequence is as follows: Pb(II) (91%) > Cd(II) (91%) > Cu(II) (86%) > Cr(III) (86%). It can be seen that the modified seaweed can enhance the removal of all the four heavy metals studied to some extents [1% for Pb(II), 3% for Cd(II) and 9% for Cr(III)]. However both non-modified and modified seaweeds could be used for treatment of the four heavy metals in industrial wastewater. The effect of pH of solution by non-modified seaweed was similar to that of modified seaweed.

Table 3.24 Effect of pH of solution on lead(II) adsorption by modified seaweed

pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\bar{X}$	% Ad
2.0	0.1002 0.1005 0.1004	40.00 40.00 40.00	9.16 9.14 9.16	30.84 30.86 30.85	15.39 15.35 15.36	15.37±0.02	77
2.5	0.1006 0.1003 0.1004	40.00 40.00 40.00	5.66 5.82 5.77	34.34 34.18 34.23	17.07 17.04 17.05	17.05±0.02	85
3.0	0.1001 0.1007 0.1005	40.00 40.00 40.00	3.65 3.75 3.69	36.35 36.26 36.31	18.16 18.00 18.07	18.08±0.08	91
3.5	0.1006 0.1003 0.1001	40.00 40.00 40.00	3.53 3.43 3.53	36.47 36.57 36.47	18.12 18.23 18.22	18.19±0.06	91
4.0	0.1007 0.1002 0.1008	40.00 40.00 40.00	3.62 3.64 3.69	36.38 36.36 36.31	18.06 18.14 18.01	18.07±0.07	91
4.5	0.1006 0.1003 0.1002	40.00 40.00 40.00	3.72 3.69 3.68	36.28 36.31 36.32	18.03 18.10 18.13	18.09±0.05	91
5.0	0.1009 0.1005 0.1007	40.00 40.00 40.00	3.82 3.77 3.74	36.18 36.23 36.26	17.93 18.02 18.00	17.99±0.05	91

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.25 Effect of pH of solution on copper(II) adsorption by modified seaweed

pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
2.0	0.1004 0.1005 0.1004	15.00 15.00 15.00	5.27 5.12 5.54	9.73 9.88 9.46	4.85 4.92 4.71	4.82±0.10	66
2.5	0.1002 0.1002 0.1004	15.00 15.00 15.00	3.58 3.58 3.65	11.42 11.43 11.35	5.70 5.70 5.65	5.68±0.03	76
3.0	0.1001 0.1005 0.1007	15.00 15.00 15.00	2.28 2.30 2.24	12.72 12.70 12.76	6.35 6.32 6.33	6.34±0.02	85
3.5	0.1003 0.1003 0.1004	15.00 15.00 15.00	2.13 2.13 2.11	12.87 12.88 12.90	6.42 6.42 6.42	6.42±0.00	86
4.0	0.1007 0.1004 0.1008	15.00 15.00 15.00	2.25 2.27 2.22	12.75 12.73 12.78	6.33 6.34 6.34	6.34±0.01	85
4.5	0.1003 0.1004 0.1002	15.00 15.00 15.00	2.35 2.46 2.42	12.65 12.55 12.58	6.30 6.25 6.28	6.28±0.03	84
5.0	0.1008 0.1006 0.1007	15.00 15.00 15.00	2.44 2.46 2.45	12.57 12.54 12.55	6.23 6.23 6.23	6.23±0.00	84

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.26 Effect of pH of solution on cadmium(II) adsorption by modified seaweed

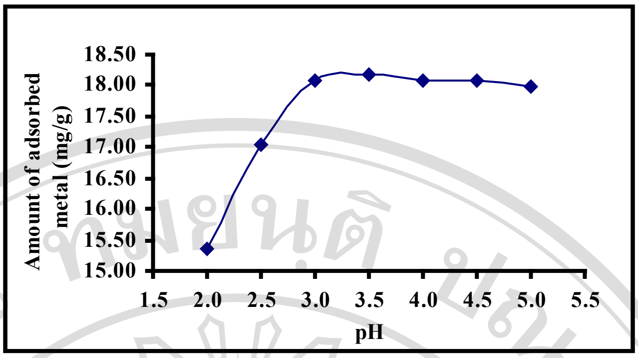
pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
2.0	0.1003 0.1002 0.1004	25.00 25.00 25.00	6.01 6.06 6.04	18.99 18.94 18.96	9.47 9.45 9.44	9.45±0.01	76
2.5	0.1003 0.1002 0.1003	25.00 25.00 25.00	5.11 5.16 5.16	19.89 19.85 19.84	9.91 9.90 9.89	9.90±0.01	79
3.0	0.1001 0.1004 0.1002	25.00 25.00 25.00	2.68 2.65 2.68	22.32 22.35 22.32	11.15 11.13 11.14	11.14±0.01	89
3.5	0.1002 0.1003 0.1003	25.00 25.00 25.00	2.24 2.26 2.23	22.76 22.74 22.77	11.36 11.33 11.35	11.35±0.01	91
4.0	0.1002 0.1003 0.1004	25.00 25.00 25.00	2.42 2.46 2.49	22.59 22.54 22.51	11.27 11.24 11.21	11.24±0.03	90
4.5	0.1003 0.1002 0.1002	25.00 25.00 25.00	2.50 2.46 2.46	22.50 22.54 22.54	11.22 11.25 11.25	11.24±0.02	90
5.0	0.1003 0.1005 0.1002	25.00 25.00 25.00	2.38 2.38 2.41	22.62 22.62 22.59	11.28 11.25 11.27	11.27±0.01	90

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

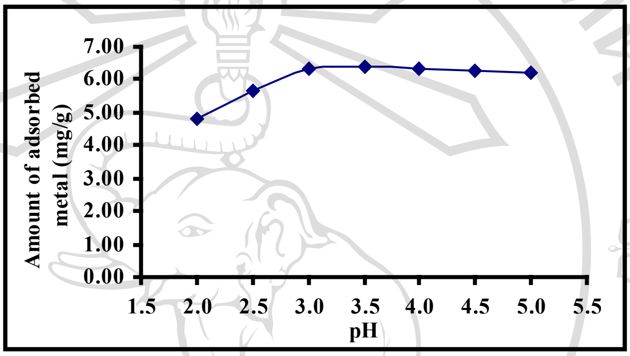
Table 3.27 Effect of pH of solution on chromium(III) adsorption by modified seaweed

pH	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\bar{X}$	% Ad
2.0	0.1006 0.1005 0.1004	15.00 15.00 15.00	6.50 6.48 6.50	8.50 8.52 8.50	4.22 4.24 4.24	4.23±0.01	57
2.5	0.1002 0.1005 0.1004	15.00 15.00 15.00	3.72 3.69 3.68	11.28 11.31 11.32	5.63 5.63 5.64	5.63±0.01	75
3.0	0.1002 0.1005 0.1004	15.00 15.00 15.00	2.18 2.19 2.12	12.82 12.81 12.88	6.40 6.37 6.41	6.39±0.02	86
3.5	0.1002 0.1001 0.1002	15.00 15.00 15.00	2.38 2.41 2.38	12.62 12.59 12.62	6.30 6.29 6.30	6.29±0.00	84
4.0	0.1003 0.1002 0.1004	15.00 15.00 15.00	2.37 2.43 2.48	12.63 12.57 12.52	6.30 6.27 6.24	6.27±0.03	84
4.5	0.1003 0.1003 0.1002	15.00 15.00 15.00	2.40 2.42 2.39	12.60 12.58 12.61	6.28 6.27 6.29	6.28±0.01	84
5.0	0.1001 0.1002 0.1001	15.00 15.00 15.00	2.38 2.38 2.41	12.62 12.62 12.59	6.31 6.30 6.29	6.30±0.01	84

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption



(a)



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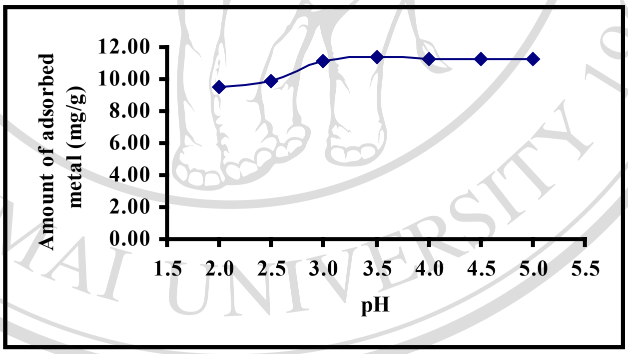

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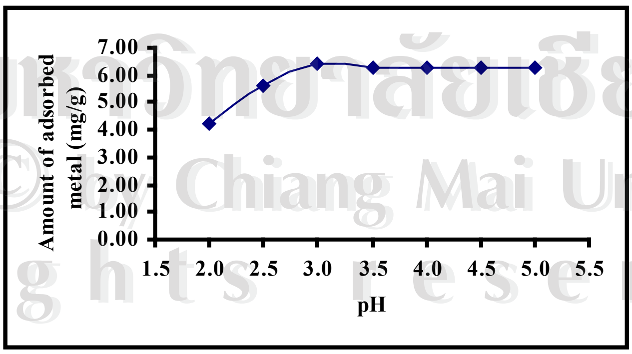


(d)

Figure 3.6 Effect of pH of solution on (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) adsorption by modified seaweed

The removal of metal ions in aqueous and wastewater are highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the speciation of the species. The seaweed was modified by crosslink-xanthatemethod. The hydroxly groups in cellulose and alginate were substituted to xanthate groups.[20]

$$R\text{-}OH + S{=}C{=}S + NaOH \longrightarrow R\text{-}OC({=}S)SNa + H_2O$$

Xanthate group is replaced by a heavy metal ion.

$$R\text{-}OC({=}S)SNa + M^{+} \longrightarrow R\text{-}OC({=}S)SM + Na^{+}$$

In the same way of non-modified seaweed, pH of the solution affected the adsorption of the sorbent by the competition of the hydronium ions and metal ions. The active sites of the sorbent adsorb the hydronium ions rather than the metal ions at the low pH. In this case the interaction forces between the hydronium and metal ions is not considered.

With the high pH (greater than 5), the metal ion in the solution will precipitation with the hydroxide ion. So the experiment was limited the range of pH parameter studied form 2 to 5 (step 0.5).

3.3.2 Effect of shaking time

As mentioned in section 3.2.3 shaking time is one of the most important parameters for any sorption process. The shaking time should be sufficient for complete sorption to be occurred. The kinetics of the sorption process to attain the equilibrium depends on the shaking time. Therefore, the same optimization of shaking time procedure used for the non-modified seaweed was repeated for the modified seaweed for the removal of Pb(II), Cu(II), Cd(II) and Cr(III).

The effect of shaking time on adsorption of lead(II), chromium(III) copper(II) and cadmium(II) on modified seaweed was studied as in Tables 3.8-3.31 and Figure 3.7. The adsorption occurred in two phases; an initial phase occurred quickly in first 20 min, the slower second phase continued until the end of the experimental period. The equilibrium was reached within 60 min. At equilibrium, the adsorption of the four heavy metals studied on the modified biosorbent falls into the follwing decreasing order: Pb(II) (91%) > Cd(II) (91%) > Cu(II) (86%) > Cr(III) (85%) whereas that for the non-modified one is Pb(II) (88%) > Cd(II) (83%) > Cr(III) (75%) > Cu(II) (72%). The enhancement in adsorption of the four heavy metals studided can be obtained using the modified seaweed which are 3% for Pb(II), 8% for Cd(II), 14% for Cu(II) and 10% for Cr(III). Again, this implies that simultaneous removal of the above four heavy metals may be possible based on sorption of the metal ions on the non-modified and/or modified seaweed.

The effect of shaking time also has a role in the adsorption kinetics. The modified cell surface and the modified active site results in the same adsorption phenomena as those of the non-modified one. Rapid adsorption is obtained at the beginning and increase slowly before reaching equilibrium. From the pattern of the adsorption, this may occur in other adsorption system even mono or hetero-element.

As the adsorption with the modified seaweed yielded more than the non-modified one with equal shaking time. The efficiency of the modified seaweed is greater than that of non-modified seaweed.

Table 3.28 Effect of shaking time on lead(II) adsorption by modified seaweed

Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe		% Ad
					(mg/g)	$\overline{X}$	
5	0.1003 0.1004 0.1002	40.00 40.00 40.00	13.16 13.19 13.20	26.84 26.81 26.80	13.38 13.35 13.37	13.37±0.01	67
10	0.1002 0.1002 0.1004	40.00 40.00 40.00	11.59 11.69 11.63	28.41 28.31 28.37	14.18 14.13 14.13	14.14±0.03	71
20	0.1002 0.1003 0.1003	40.00 40.00 40.00	7.60 7.53 7.60	32.40 32.47 32.40	16.17 16.19 16.15	16.17±0.02	81
30	0.1004 0.1002 0.1003	40.00 40.00 40.00	5.36 5.43 5.40	34.64 34.57 34.60	17.25 17.25 17.25	17.25±0.00	86
60	0.1004 0.1005 0.1002	40.00 40.00 40.00	3.49 3.51 2.53	36.51 36.49 37.47	18.18 18.15 18.70	18.34±0.31	91
90	0.1001 0.1002 0.1002	40.00 40.00 40.00	3.51 3.51 3.51	36.49 36.49 36.49	18.23 18.21 18.21	18.21±0.01	91
120	0.1003 0.1002 0.1002	40.00 40.00 40.00	3.53 3.51 3.52	36.47 36.49 36.48	18.18 18.21 18.20	18.20±0.01	91

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.29 Effect of shaking time on copper(II) adsorption by modified seaweed

Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\bar{X}$	% Ad
5	0.1003 0.1005 0.1002	15.00 15.00 15.00	5.56 5.65 5.65	9.44 9.35 9.35	4.70 4.65 4.67	4.67±0.03	62
10	0.1003 0.1002 0.1004	15.00 15.00 15.00	4.11 4.14 4.17	10.89 10.86 10.83	5.43 5.42 5.39	5.41±0.02	72
20	0.1002 0.1002 0.1003	15.00 15.00 15.00	3.66 3.69 3.68	11.34 11.31 11.32	5.66 5.64 5.64	5.65±0.01	75
30	0.1004 0.1002 0.1003	15.00 15.00 15.00	2.72 2.73 2.73	12.28 12.27 12.27	6.12 6.12 6.12	6.12±0.00	82
60	0.1006 0.1004 0.1002	15.00 15.00 15.00	2.08 2.10 2.09	12.92 12.90 12.91	6.42 6.43 6.44	6.43±0.01	86
90	0.1003 0.1003 0.1004	15.00 15.00 15.00	2.11 2.11 2.11	12.89 12.89 12.89	6.43 6.42 6.42	6.42±0.00	86
120	0.1004 0.1002 0.1003	15.00 15.00 15.00	2.06 2.10 2.08	12.94 12.90 12.92	6.45 6.44 6.44	6.44±0.00	86

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.30 Effect of shaking time on cadmium(II) adsorption by modified seaweed

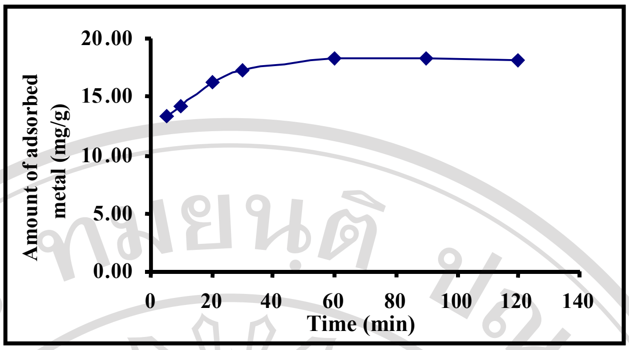
Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\bar{X}$	% Ad
5	0.1002 0.1004 0.1002	25.00 25.00 25.00	4.77 4.85 4.86	20.23 20.15 20.14	10.10 10.04 10.05	10.06±0.03	81
10	0.1005 0.1002 0.1001	25.00 25.00 25.00	3.54 3.58 3.60	21.47 21.42 21.40	10.68 10.69 10.69	10.69±0.01	86
20	0.1003 0.1002 0.1002	25.00 25.00 25.00	2.76 2.77 2.77	22.24 22.23 22.23	11.09 11.09 11.09	11.09±0.00	89
30	0.1001 0.1004 0.1004	25.00 25.00 25.00	2.43 2.47 2.43	22.57 22.54 22.57	11.27 11.22 11.24	11.25±0.03	90
60	0.1005 0.1003 0.1002	25.00 25.00 25.00	2.23 2.26 2.25	22.77 22.74 22.75	11.33 11.34 11.35	11.34±0.01	91
90	0.1001 0.1003 0.1004	25.00 25.00 25.00	2.21 2.22 2.20	22.79 22.78 22.80	11.38 11.36 11.35	11.36±0.02	91
120	0.1002 0.1003 0.1003	25.00 25.00 25.00	2.24 2.22 2.25	22.76 22.79 22.75	11.36 11.36 11.34	11.35±0.01	91

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption

Table 3.31 Effect of shaking time on chromium(III) adsorption by modified seaweed

Time (min)	Weight (g)	Ci (mg/l)	Ce (mg/l)	Cad (mg/l)	qe (mg/g)	qe $\overline{X}$	% Ad
5	0.1003 0.1005 0.1002	15.00 15.00 15.00	6.13 6.15 6.19	8.87 8.85 8.81	4.42 4.40 4.40	4.41±0.01	59
10	0.1001 0.1003 0.1002	15.00 15.00 15.00	5.44 5.48 5.46	9.56 9.52 9.54	4.78 4.75 4.76	4.76±0.01	63
20	0.1002 0.1002 0.1004	15.00 15.00 15.00	4.34 4.36 4.36	10.67 10.64 10.64	5.32 5.31 5.30	5.31±0.01	71
30	0.1003 0.1002 0.1001	15.00 15.00 15.00	3.15 3.16 3.21	11.85 11.84 11.79	5.91 5.91 5.89	5.90±0.01	79
60	0.1006 0.1005 0.1002	15.00 15.00 15.00	2.17 2.19 2.22	12.83 12.82 12.78	6.38 6.38 6.38	6.38±0.00	85
90	0.1002 0.1004 0.1003	15.00 15.00 15.00	2.18 2.21 2.22	12.82 12.79 12.78	6.40 6.37 6.37	6.38±0.02	85
120	0.1004 0.1001 0.1002	15.00 15.00 15.00	2.20 2.25 2.24	12.81 12.76 12.76	6.38 6.37 6.37	6.37±0.00	85

Ci: initial concentration, Ce: residual concentration, Cad: adsorbed concentration, qe: amount of metal ions adsorbed per gram seaweed, %Ad: percentage of adsorption



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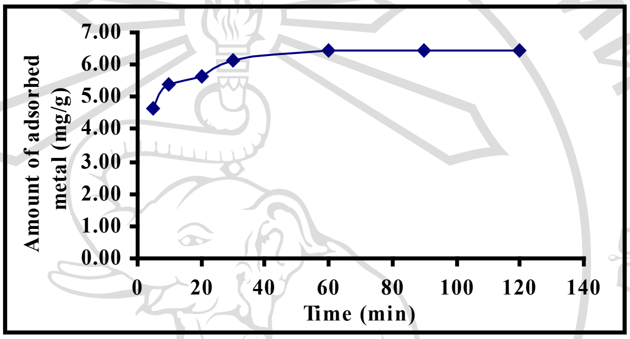

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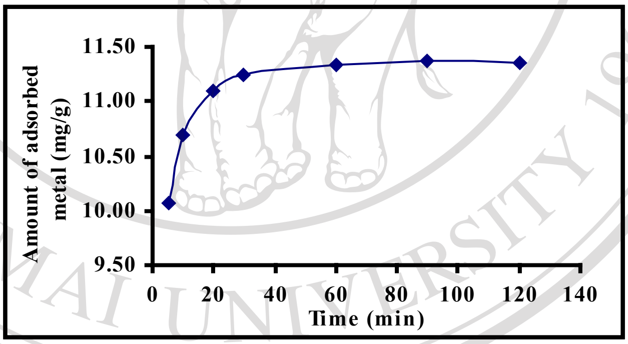
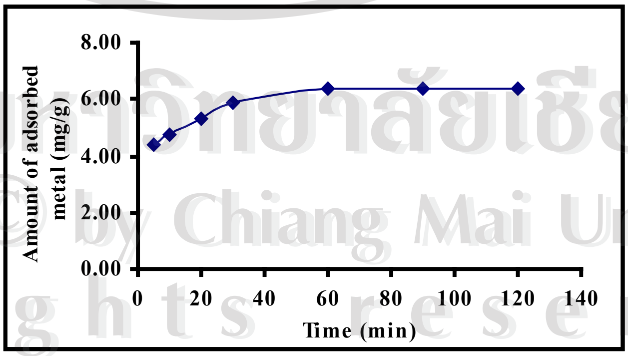


(c)



(d)

Figure 3.7 Effect of shaking time on (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) adsorption by non-modified seaweed

3.3.3 Effect of other metals

Previous investigations indicate that both non-modified and modified seaweed with the particle sizes of 0.21-0.36 mm can be used as biosorbents for Pb(II), Cu(II), Cd(II) and Cr(III) rather satisfactorily. The poor selectivity of both biosorbents may lead to the simultaneous removal of these four heavy metals in aqueous solution.

The low selectivity of modified seaweed for the four heavy metal ions was investigated in binary, ternary and quaternary systems. The experiment was done by varied the ratio of target ion and competitive in solution and uptake by modified seaweed. The amount of main ion adsorbed was decreased when the concentration of co-ion increased. All studied metal species could be removed simultaneously by the modified seaweed.

The results from effect of other metals were shown in Table 3.31-3.34. It was found that each target metal ion sorbed on the biosorbent in the present of other metal ions in binary, ternary and quaternary mixtures would decrease owing to the competitive effect. However, adsorption of Pb(II) on the non-modified seaweed and Cd(II) on the modified seaweed are the greatest. However the amounts of each target metal adsorbed on the biosorbents in the mixture are lined according to the following decreasing order: for the modified seaweed: Cd(II) > Pb(II) > Cr(III) > Cu(II) for the non-modified one: Pb(II) > Cd(II) > Cr(III) > Cu(II). The amounts of each metal adsorbent on the modified seaweed are greater than that obtained by using the non-modified one as biosorbent.[21]

Table 3.32 Effect of copper(II), cadmium(II) and chromium(III) on lead(II) adsorption

Target metal : competitive metals Ratio	Amount of Pb(II) adsorbed (mg/g)	Average amount of Pb(II) adsorbed (mg/g)	% Adsorption efficiency
Pb(II)	4.80 4.77 4.80	4.79	-
Pb(II):Cu(II) 1.0 : 0.5	4.46 4.45 4.51	4.47	-7
Pb(II):Cu(II) 1.0 : 1.0	4.33 4.32 4.29	4.31	-10
Pb(II):Cu(II) 1.0 : 1.5	4.19 4.23 4.23	4.22	-12
Pb(II):Cr(III) 1.0 : 0.5	4.49 4.50 4.51	4.50	-6
Pb(II):Cr(III) 1.0 : 1.0	4.37 4.34 4.33	4.35	-9
Pb(II):Cr(III) 1.0 : 1.5	4.24 4.24 4.22	4.23	-12
Pb(II):Cd(II) 1.0 : 0.5	4.41 4.43 4.44	4.42	-8
Pb(II):Cd(II) 1.0 : 1.0	4.27 4.31 4.33	4.30	-10
Pb(II):Cd(II) 1.0 : 1.5	4.12 4.16 4.15	4.14	-13

Table 3.32 Effect of copper(II), cadmium(II) and chromium(III) on lead(II) adsorption (continue)

Target metal : competitive metals Ratio	Amount of Pb(II) adsorbed (mg/g)	Average amount of Pb(II) adsorbed (mg/g)	% Adsorption efficiency
Pb(II): Cd(II):Cu(II) 1.0 : 0.5 : 0.5	4.31 4.29 4.32	4.31	-10
Pb(II): Cd(II):Cu(II) 1.0 : 1.0 : 1.0	4.19 4.17 4.21	4.19	-12
Pb(II): Cd(II):Cu(II) 1.0 : 1.5 : 1.5	4.01 4.02 4.03	4.02	-16
Pb(II):Cr(III):Cu(II) 1.0 : 0.5 : 0.5	4.34 4.35 4.36	4.35	-9
Pb(II):Cr(III):Cu(II) 1.0 : 1.0 : 1.0	4.20 4.15 4.23	4.19	-12
Pb(II):Cr(III):Cu(II) 1.0 : 1.5 : 1.5	4.05 4.08 4.07	4.07	-15
Pb(II):Cr(III):Cd(II) 1.0 : 0.5 : 0.5	4.28 4.30 4.30	4.29	-10
Pb(II):Cr(III):Cd(II) 1.0 : 1.0 : 1.0	4.14 4.13 4.14	4.13	-14
Pb(II):Cr(III):Cd(II) 1.0 : 1.5 : 1.5	4.01 4.00 4.02	4.01	-16
Pb(II):Cr(III):Cd(II):Cu(II) 1.0 : 0.5 : 0.5 : 0.5	4.17 4.16 4.19	4.17	-13
Pb(II):Cr(III):Cd(II):Cu(II) 1.0 : 1.0 : 1.0 : 1.0	3.99 4.05 4.02	4.02	-16
Pb(II):Cr(III):Cd(II):Cu(II) 1.0 : 1.5 : 1.5 : 1.5	3.83 3.82 3.81	3.82	-20

Table 3.33 Effect of lead(II), cadmium(II) and chromium(III) on copper(II) adsorption

Target metal : competitive metals Ratio	Amount of Cu(II) adsorbed (mg/g)	Average amount of Cu(II) adsorbed (mg/g)	% Adsorption efficiency
Cu(II)	4.42 4.37 4.35	4.38	-
Cu(II):Cr(III) 1.0 : 0.5	3.47 3.50 3.53	3.50	-20
Cu(II):Cr(III) 1.0 : 1.0	3.34 3.32 3.32	3.33	-24
Cu(II):Cr(III) 1.0 : 1.5	3.16 3.15 3.13	3.15	-28
Cu(II):Cd(II) 1.0 : 0.5	3.57 3.54 3.53	3.55	-19
Cu(II):Cd(II) 1.0 : 1.0	3.47 3.40 3.42	3.43	-22
Cu(II):Cd(II) 1.0 : 1.5	3.29 3.25 3.29	3.28	-25
Cu(II):Pb(II) 1.0 : 0.5	3.43 3.49 3.50	3.47	-21
Cu(II):Pb(II) 1.0 : 1.0	3.31 3.31 3.34	3.32	-24
Cu(II):Pb(II) 1.0 : 1.5	3.13 3.15 3.16	3.15	-28

Table 3.33 Effect of lead(II), cadmium(II) and chromium(III) on copper(II) adsorption (continue)

Target metal : competitive metals Ratio	Amount of Cu(II) adsorbed (mg/g)	Average amount of Cu(II) adsorbed (mg/g)	% Adsorption efficiency
Cu(II):Pb(II): Cd(II) 1.0 : 0.5 : 0.5	3.37 3.39 3.33	3.36	-23
Cu(II):Pb(II): Cd(II) 1.0 : 1.0 : 1.0	3.22 3.21 3.24	3.22	-26
Cu(II):Pb(II): Cd(II) 1.0 : 1.5 : 1.5	3.04 3.03 3.02	3.03	-31
Cu(II):Pb(II):Cr(III) 1.0 : 0.5 : 0.5	3.20 3.18 3.24	3.21	-27
Cu(II):Pb(II):Cr(III) 1.0 : 1.0 : 1.0	3.05 3.06 3.07	3.06	-30
Cu(II):Pb(II):Cr(III) 1.0 : 1.5 : 1.5	2.89 2.90 2.86	2.88	-34
Cu(II):Cr(III):Cd(II) 1.0 : 0.5 : 0.5	3.29 3.32 3.28	3.30	-25
Cu(II):Cr(III):Cd(II) 1.0 : 1.0 : 1.0	3.11 3.14 3.06	3.10	-29
Cu(II):Cr(III):Cd(II) 1.0 : 1.5 : 1.5	2.84 2.85 2.84	2.84	-35
Cu(II):Pb(II):Cr(III):Cd(II) 1.0 : 0.5 : 0.5 : 0.5	3.21 3.18 3.20	3.20	-27
Cu(II):Pb(II):Cr(III):Cd(II) 1.0 : 1.0 : 1.0 : 1.0	3.08 3.09 3.06	3.07	-30
Cu(II):Pb(II):Cr(III):Cd(II) 1.0 : 1.5 : 1.5 : 1.5	2.71 2.73 2.70	2.71	-38

Table 3.34 Effect of lead(II), copper(II) and chromium(III) on cadmium(II) adsorption

Target metal : competitive metals Ratio	Amount of Cd(II) adsorbed (mg/g)	Average amount of Cd(II) adsorbed (mg/g)	% Adsorption efficiency
Cd(II)	4.85 4.84 4.85	4.85	-
Cd(II):Cr(III) 1.0 : 0.5	4.76 4.74 4.78	4.76	-2
Cd(II):Cr(III) 1.0 : 1.0	4.63 4.65 4.68	4.66	-4
Cd(II):Cr(III) 1.0 : 1.5	4.45 4.43 4.44	4.44	-8
Cd(II):Cu(II) 1.0 : 0.5	4.79 4.76 4.78	4.78	-1
Cd(II):Cu(II) 1.0 : 1.0	4.61 4.62 4.64	4.63	-4
Cd(II):Cu(II) 1.0 : 1.5	4.41 4.42 4.45	4.42	-9
Cd(II):Pb(II) 1.0 : 0.5	4.75 4.79 4.78	4.77	-1
Cd(II):Pb(II) 1.0 : 1.0	4.60 4.61 4.61	4.60	-5
Cd(II):Pb(II) 1.0 : 1.5	4.38 4.40 4.42	4.40	-9

Table 3.34 Effect of lead(II), copper(II) and chromium(III) on cadmium(II) adsorption (continue)

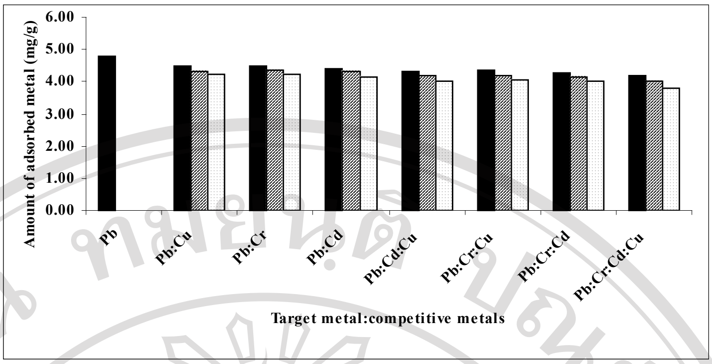
Target metal : competitive metals Ratio	Amount of Cd(II) adsorbed (mg/g)	Average amount of Cd(II) adsorbed (mg/g)	% Adsorption efficiency
Cd(II):Pb(II): Cu(II) 1.0 : 0.5 : 0.5	4.69 4.71 4.72	4.71	-3
Cd(II):Pb(II): Cu(II) 1.0 : 1.0 : 1.0	4.56 4.57 4.56	4.56	-6
Cd(II):Pb(II): Cu(II) 1.0 : 1.5 : 1.5	4.35 4.37 4.34	4.35	-10
Cd(II):Pb(II):Cr(III) 1.0 : 0.5 : 0.5	4.65 4.67 4.66	4.66	-4
Cd(II):Pb(II):Cr(III) 1.0 : 1.0 : 1.0	4.47 4.49 4.50	4.49	-7
Cd(II):Pb(II):Cr(III) 1.0 : 1.5 : 1.5	4.35 4.33 4.31	4.33	-11
Cd(II):Cr(III):Cu(II) 1.0 : 0.5 : 0.5	4.65 4.66 4.69	4.67	-4
Cd(II):Cr(III):Cu(II) 1.0 : 1.0 : 1.0	4.50 4.54 4.52	4.52	-7
Cd(II):Cr(III):Cu(II) 1.0 : 1.5 : 1.5	4.33 4.34 4.35	4.34	-10
Cd(II):Pb(II):Cr(III):Cu(II) 1.0 : 0.5 : 0.5 : 0.5	4.51 4.50 4.55	4.52	-7
Cd(II):Pb(II):Cr(III):Cu(II) 1.0 : 1.0 : 1.0 : 1.0	4.42 4.38 4.35	4.38	-10
Cd(II):Pb(II):Cr(III):Cu(II) 1.0 : 1.5 : 1.5 : 1.5	4.19 4.19 4.20	4.19	-13

Table 3.35 Effect of lead(II), copper(II) and cadmium(II) on chromium(III) adsorption

Target metal : competitive metals Ratio	Amount of Cr (III) adsorbed (mg/g)	Average amount of Cr(III) adsorbed (mg/g)	% Adsorption efficiency
Cr(III)	3.94 3.92 3.91	3.92	-
Cr(III):Cu(II) 1.0 : 0.5	3.92 3.94 3.88	3.92	-
Cr(III):Cu(II) 1.0 : 1.0	3.60 3.65 3.64	3.63	-7
Cr(III):Cu(II) 1.0 : 1.5	3.36 3.35 3.37	3.36	-14
Cr(III):Cd(II) 1.0 : 0.5	3.70 3.67 3.69	3.69	-6
Cr(III):Cd(II) 1.0 : 1.0	3.59 3.58 3.57	3.58	-9
Cr(III):Cd(II) 1.0 : 1.5	3.40 3.39 3.37	3.39	-14
Cr(III):Pb(II) 1.0 : 0.5	3.88 3.90 3.88	3.89	-1
Cr(III):Pb(II) 1.0 : 1.0	3.77 3.73 3.67	3.72	-5
Cr(III):Pb(II) 1.0 : 1.5	3.59 3.58 3.56	3.57	-9

Table 3.35 Effect of lead(II), copper(II) and cadmium(II) on chromium(III) adsorption(continue)

Target metal : competitive metals Ratio	Amount of Cr (III) adsorbed (mg/g)	Average amount of Cr(III) adsorbed (mg/g)	% Adsorption efficiency
Cr(III):Pb(II): Cd(II) 1.0 : 0.5 : 0.5	3.62 3.61 3.59	3.61	-8
Cr(III):Pb(II): Cd(II) 1.0 : 1.0 : 1.0	3.42 3.45 3.41	3.42	-13
Cr(III):Pb(II): Cd(II) 1.0 : 1.5 : 1.5	3.23 3.24 3.25	3.24	-17
Cr(III):Pb(II):Cu(II) 1.0 : 0.5 : 0.5	3.61 3.62 3.63	3.62	-8
Cr(III):Pb(II):Cu(II) 1.0 : 1.0 : 1.0	3.37 3.41 3.41	3.40	-13
Cr(III):Pb(II):Cu(II) 1.0 : 1.5 : 1.5	3.16 3.19 3.18	3.18	-19
Cr(III):Cd(II):Cu(II) 1.0 : 0.5 : 0.5	3.64 3.64 3.66	3.65	-7
Cr(III):Cd(II):Cu(II) 1.0 : 1.0 : 1.0	3.49 3.46 3.45	3.47	-12
Cr(III):Cd(II):Cu(II) 1.0 : 1.5 : 1.5	3.22 3.25 3.26	3.24	-17
Cr(III):Pb(II):Cd(II):Cu(II) 1.0 : 0.5 : 0.5 : 0.5	3.50 3.52 3.51	3.51	-10
Cr(III):Pb(II):Cd(II):Cu(II) 1.0 : 1.0 : 1.0 : 1.0	3.35 3.35 3.40	3.37	-14
Cr(III):Pb(II):Cd(II):Cu(II) 1.0 : 1.5 : 1.5 : 1.5	3.20 3.18 3.17	3.18	-19



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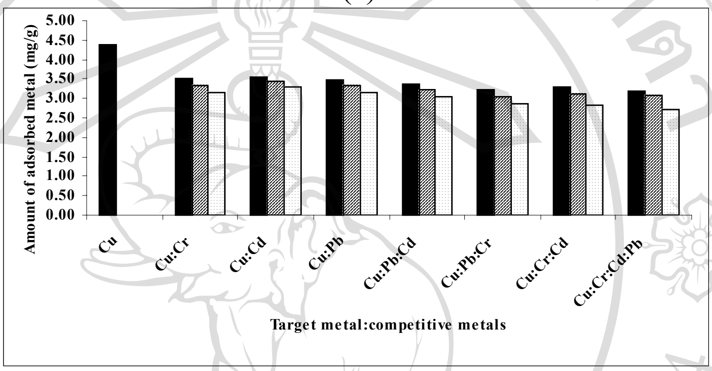

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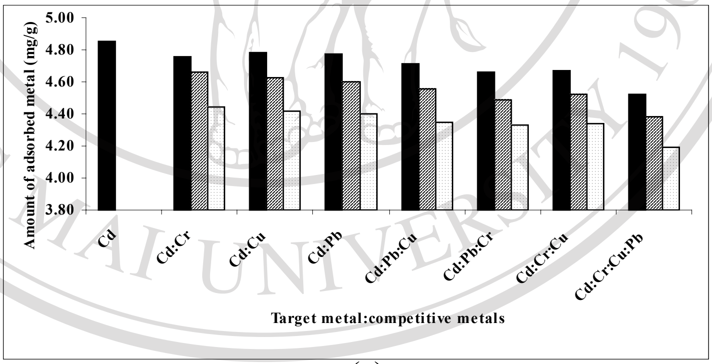

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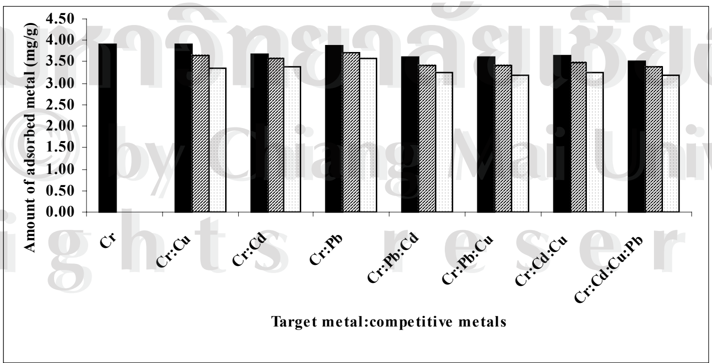


(d)

Figure 3.8 Effect of competitive metals on (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) adsorption by modified seaweed

Target:Competitive = 1.0:0.5 Target:Competitive = 1.0:1.0 Target:Competitive = 1.0:1.5

3.3.4 Performance characteristics of modified seaweed

The adsorption isotherms were studied at various concentrations of lead(II) (30-80 mg/l), copper(II)(10-30 mg/l), cadmium(II)(20-40mg/l) and chromium(III) (10-30mg/l). The Langmuir and Freundlich adsorption isotherms of each metal ion were shown in Tables 3.36-3.39 and Figures 3.9-3.10. The Langmuir adsorption isotherm constant was calculated by the y-intercept and slope of a graph plotting by $1/q_e$ versus $1/C_e$. The Freundlich adsorption isotherm constant was obtained by ploting log q_e against log C_e. The Langmuir and Freundlich adsorption constants from the isotherms with the correlation coefficients were also given in Tables 3.40-3.41.

Table 3.36 Adsorption of lead(II) by modified seaweed

C_i (mg/l)	C_e (mg/l)	q_e (mg/g)	$1/C_e$	$1/q_e$	log C_e	log q_e
30.00	2.25	13.83	0.45	0.07	0.35	1.14
35.00	2.92	15.95	0.34	0.06	0.47	1.20
40.00	3.55	18.18	0.28	0.06	0.55	1.26
45.00	4.25	20.31	0.24	0.05	0.63	1.31
50.00	4.83	22.53	0.21	0.04	0.68	1.35
60.00	7.48	26.18	0.13	0.04	0.87	1.42
70.00	12.58	28.59	0.08	0.04	1.10	1.46
80.00	16.34	31.77	0.06	0.03	1.21	1.50

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed,

Table 3.37 Adsorption of copper(II) by modified seaweed

C_i (mg/l)	C_e (mg/l)	q_e (mg/g)	$1/C_e$	$1/q_e$	log C_e	log q_e
10.00	1.02	4.48	0.99	0.22	0.01	0.65
15.00	1.52	6.72	0.66	0.15	0.18	0.83
20.00	2.16	8.90	0.46	0.11	0.34	0.95
25.00	2.67	11.12	0.37	0.09	0.43	1.05
30.00	3.32	13.29	0.30	0.08	0.52	1.13

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed

Table 3.38 Adsorption of cadmium(II) by modified seaweed

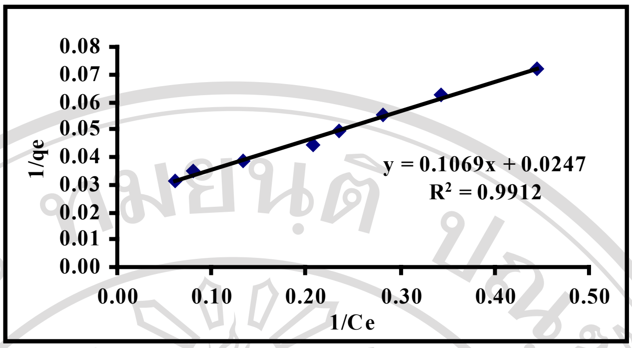
C_i (mg/l)	C_e (mg/l)	q_e (mg/g)	$1/C_e$	$1/q_e$	log C_e	log q_e
20.00	1.58	9.18	0.63	0.11	0.20	0.96
25.00	1.86	11.52	0.54	0.09	0.27	1.06
30.00	2.29	13.81	0.44	0.07	0.36	1.14
35.00	2.65	16.10	0.38	0.06	0.42	1.21
40.00	3.11	18.39	0.32	0.05	0.49	1.27

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed

Table 3.39 Adsorption of chromium(III) by modified seaweed

C_i (mg/l)	C_e (mg/l)	q_e (mg/g)	$1/C_e$	$1/q_e$	log C_e	log q_e
10.00	2.08	3.95	0.48	0.25	0.32	0.60
15.00	2.34	6.31	0.43	0.16	0.37	0.80
20.00	2.63	8.66	0.38	0.12	0.42	0.94
25.00	2.89	11.00	0.35	0.09	0.46	1.04
30.00	3.35	13.27	0.30	0.08	0.53	1.12

Ci: initial concentration, Ce: residual concentration, qe: amount of metal ions adsorbed per gram seaweed



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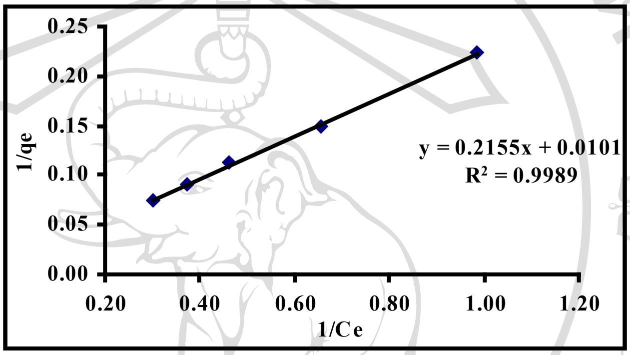

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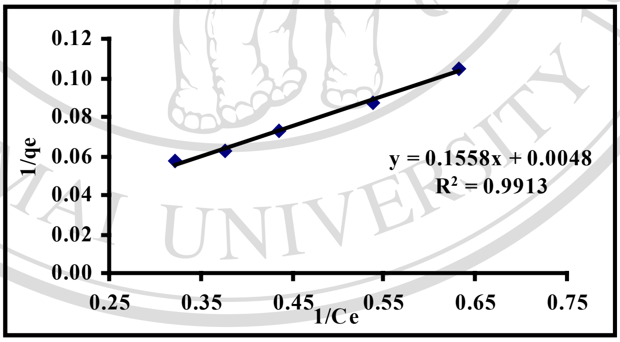

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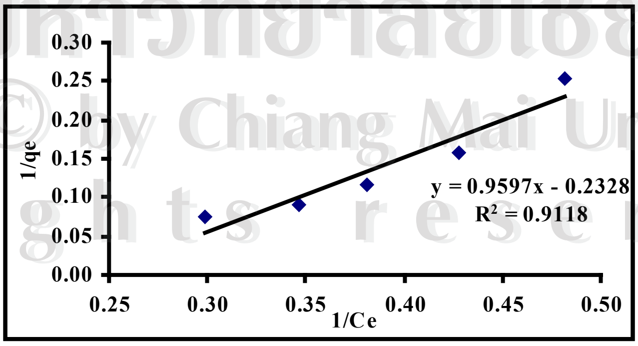

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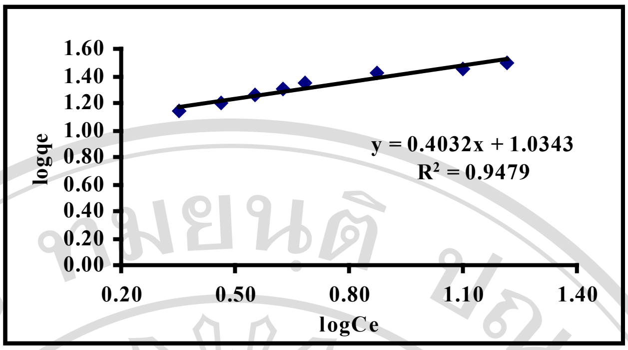
Figure 3.9 Langmuir adsorption isotherm of (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) by modified seaweed



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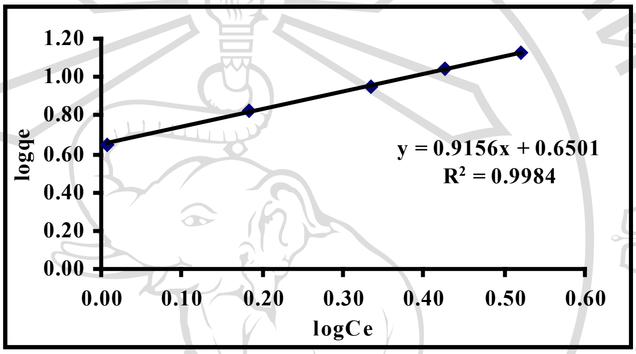

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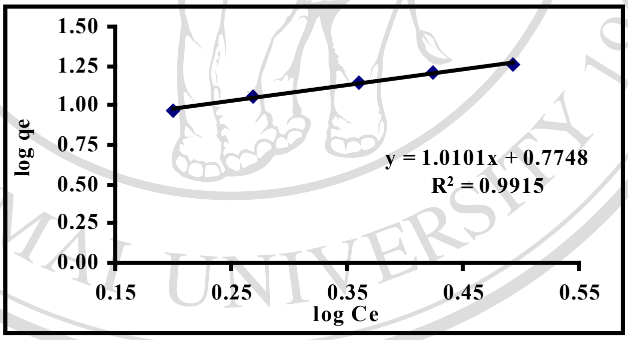

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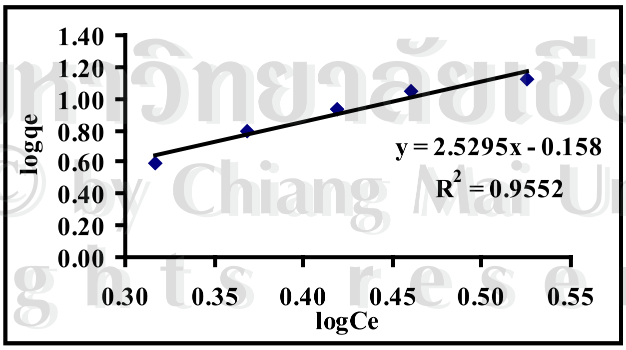


(d)

Figure 3.10 Freundlich adsorption isotherm of (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) by modified seaweed

Table3.40 The Langmuir adsorption constants obtained from the Langmuir adsorption isotherm of each metal on modified seaweed

Metal	The Langmuir adsorption constants		
	Q^o	b	R^2
Lead(II)	40.49	0.23	0.9912
Copper(II)	99.00	0.05	0.9989
Cadmium(II)	208.33	0.03	0.9913
Chromium(III)	-4.29	-0.24	0.9118

Q^o: amount of metal adsorbed per gram of dried seaweed forming a complete monolayer on the surface (mg/g)
b: Langmuir adsorption constant
R^2: correlation coefficient

Table3.41 The Freundlich adsorption constants obtained from the Langmuir adsorption isotherm of each metal on modified seaweed

Metal	The Freundlich adsorption constants		
	K_F	n	R^2
Lead(II)	10.82	2.48	0.9479
Copper(II)	4.47	1.09	0.9984
Cadmium(II)	5.95	0.99	0.9915
Chromium(III)	0.70	0.40	0.9552

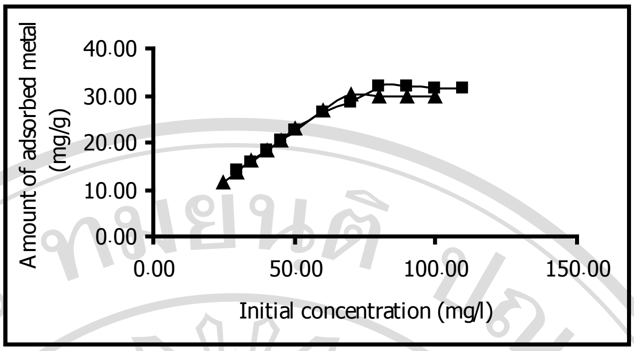
K_F : Freundlich constant representing adsorption capacity
n: Freundlich constant representing adsorption intensity
R^2: correlation coefficient

3.3.5 Adsorption capacity of non-modified seaweed and modified seaweed

The adsorption capacity was studied under the optimized conditions of pH of solution and contact time. The results obtained were shown in Table 3.42 and Figure 3.11, respectively. It was found that the amount of adsorbed metal ion increased rapidly at the early step and slightly increase before attaining a saturation value. This was defined as an adsorption capacity. Adsorption capacity of modified seaweed was higher than those of the non-modified seaweed.

Table 3.42 The adsorption capacity of metals on non-modified seaweed and modified seaweed

Metal	Adsorption capacity (mg/g)	
	Non-modified seaweed	Modified seaweed
Pb(II)	29.86±0.18	31.70±0.28
Cu(II)	18.06±0.27	23.33±0.42
Cd(III)	16.80±0.34	25.09±0.35
Cr(III)	14.83±0.27	23.66±0.69



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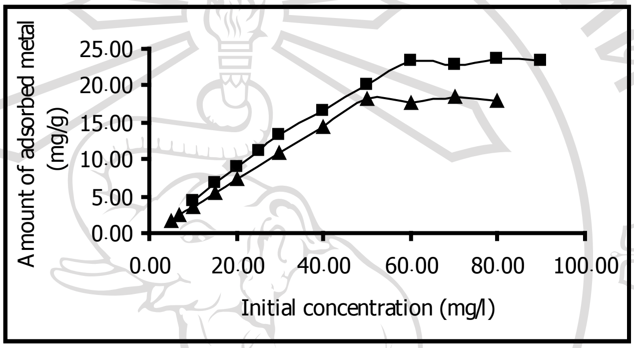

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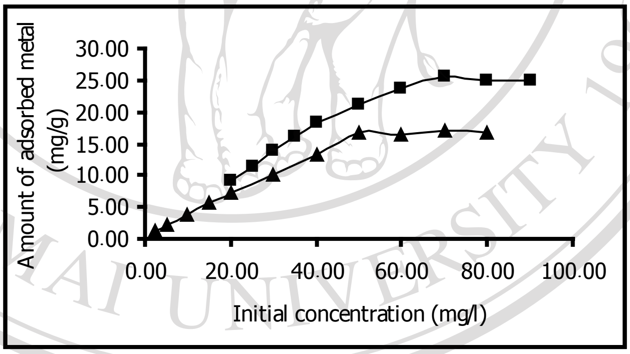

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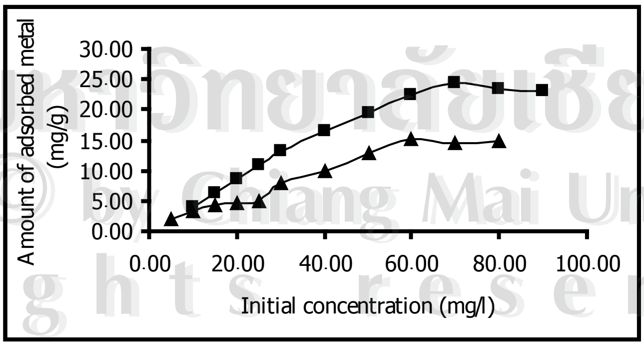

(d)

Figure 3.11 Adsorption capacity of (a) lead(II), (b) copper(II), (c) cadmium(II) and (d) chromium(III) by ▲ non-modified seaweed and ■ modified seaweed

3.3.6 Adsorption of metals in wastewater samples by non-modified seaweed and modified seaweed

The optimized conditions were applied for the removal of lead(II), copper(II), cadmium(II) and chromium(III) in wastewater samples. Both biosorbents were most effective removing binders for lead(II), copper(II), cadmium(II) and chromium(III) in wastewater samples. The results obtained are shown in Table 3.43-3.50. The biosorbent can remove the heavy metals of interest in real samples collected from plating factory (sample 1) and the treatment plant (sample 2).

Table 3.43 The adsorption of metals in wastewater sample1 by non-modified seaweed at pH 3.6

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	0.90	0.54	0.36	0.39 ± 0.07
Cu(II)	3.05	2.68	0.37	0.39 ± 0.07
Cd(II)	2.15	1.25	0.90	0.90 ± 0.03
Cr(III)	6.95	6.05	0.89	0.93 ± 0.15

* Data retrieved from 5 replicates of experiments

Table 3.44 The adsorption of metals in wastewater sample1 by non-modified seaweed at pH 3.0

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	0.90	0.52	0.38	0.36 ± 0.12
Cu(II)	3.05	2.48	0.56	0.52 ± 0.17
Cd(II)	2.15	1.68	0.51	0.55 ± 0.08
Cr(III)	6.95	6.08	0.87	0.82 ± 0.10

* Data retrieved from 5 replicates of experiments

Table 3.45 The adsorption of metals in wastewater sample1 by modified seaweed at pH 3.6

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	0.90	0.36	0.54	0.60 ± 0.11
Cu(II)	3.05	0.56	2.49	2.43 ± 0.15
Cd(II)	2.15	0.33	1.82	1.82 ± 0.01
Cr(III)	6.95	0.43	6.52	6.49 ± 0.02

* Data retrieved from 5 replicates of experiments

Table 3.46 The adsorption of metals in wastewater sample1 by modified seaweed at pH 3.0

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	0.90	0.71	0.19	0.21 ± 0.11
Cu(II)	3.05	1.37	1.68	1.65 ± 0.11
Cd(II)	2.15	1.11	1.04	1.03 ± 0.02
Cr(III)	6.95	0.65	6.30	6.30 ± 0.04

* Data retrieved from 5 replicates of experiments

Table 3.47 The adsorption of metals in wastewater sample2 by non-modified seaweed at pH 4.1

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	1.95	0.31	1.64	1.63 ± 0.04
Cu(II)	3.21	2.68	0.53	0.55 ± 0.10
Cd(II)	2.04	0.70	1.34	1.34 ± 0.02
Cr(III)	7.27	4.93	2.34	2.46 ± 0.21

* Data retrieved from 5 replicates of experiments

Table 3.48 The adsorption of metals in wastewater sample2 by non-modified seaweed at pH 3.0

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	1.95	0.38	1.57	1.58 ± 0.07
Cu(II)	3.21	2.41	0.80	0.86 ± 0.14
Cd(II)	2.04	0.84	1.20	1.19 ± 0.03
Cr(III)	7.27	4.39	2.88	2.51 ± 0.42

* Data retrieved from 5 replicates of experiments

Table 3.49 The adsorption of metals in wastewater sample2 by modified seaweed at pH 4.1

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	1.95	0.47	1.48	1.51 ± 0.09
Cu(II)	3.21	0.44	2.77	2.77 ± 0.03
Cd(II)	2.04	0.08	1.96	1.96 ± 0.02
Cr(III)	7.27	0.53	6.74	6.70 ± 0.09

* Data retrieved from 5 replicates of experiments

Table 3.50 The adsorption of metals in wastewater sample2 by modified seaweed at pH 3.0

Metal	Initial concentration (mg/l)*	Residual concentration (mg/l)*	Adsorbed concentration (mg/l)*	Amount of adsorbed metal (mg/g)*
Pb(II)	1.95	0.66	1.29	1.33 ± 0.10
Cu(II)	3.21	0.94	2.27	2.26 ± 0.02
Cd(II)	2.04	0.45	1.59	1.59 ± 0.05
Cr(III)	7.27	0.62	6.65	6.64 ± 0.02

* Data retrieved from 5 replicates of experiments